

# STATIC AND DYNAMIC MODELS FOR STAINLESS STEELMAKING IN AOD

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*by*

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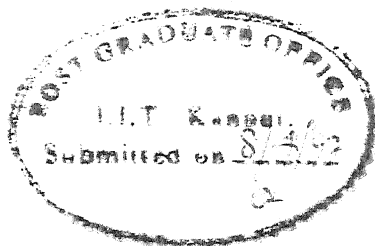


## CERTIFICATE

This is to certify that the work contained in the thesis entitled "*Static and Dynamic Models for Stainless Steelmaking in AOD*", by *S. Swaminathan*, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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## ABSTRACT

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Static and dynamic models have been developed for the Argon-Oxygen Decarburization (AOD) process of stainless steelmaking to predict carbon, chromium and temperature. Static model assumes that the oxygen potential of liquid metal remains constant throughout oxygen injection (i.e., in equilibrium with chromium oxide). The rise in the bath temperature is calculated by the heat balance calculations. The dynamic model has been developed <sup>by</sup> assuming that the mass transfer of carbon in metal phase is the rate controlling step. Three solution techniques have been developed to solve the dynamic model and are successfully tested on the data taken from literature. Static and dynamic models are first tested on the on data taken from literature and then on actual plant data. It is found that both static and dynamic models predict carbon, chromium and temperature with almost equal degree of success. The importance of adjustment parameters like average rate parameter for carbon oxidation, oxygen distribution factor for chromium oxidation and heat loss rate parameter have been discussed. It is proposed that for good predictions, an alloy dissolution model must be developed and incorporated into dynamic model. The best strategy would be to integrate the dynamic model with cost optimization model so as to produce stainless steel at lowest cost.

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(S. SWAMINATHAN)

*DEDICATED*  
*TO*  
*MY PARENTS*

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## NOMENCLATURE

$\%C$	- Carbon content in weight%
$\%Cr$	- Chromium content in weight%
$K$	- Equilibrium constant
$P_{CO}$	- Partial pressure of carbon monoxide in atmosphere
$f_C$	- Activity coefficient of carbon
$T$	- Temperature in <i>Kelvin</i>
$e_i^j$	- Interaction coefficient
$P_{total}$	- Total Pressure in atmosphere
$Q_O$	- Amount of oxygen in $m^3/ton$
$Q_d$	- Amount of diluent gas in $m^3/ton$
$t$	- Time in minutes
$\Delta H$	- Heat evolved or consumed in $KJ$
$V_t$	- Heat loss rate in $K/min$
$C_p$	- Heat capacity in $KJ/Kg.Kelvin$
$m_d$	- Moles of diluent gas in $Kmoles$
$\%C_e$	- Equilibrium carbon content in weight%
$\sigma$	- Rate parameter in $min^{-1}$
$a_{Cr}$	- Activity of chromium in the melt relative to pure solid chromium
$\gamma_C$	- Activity of coefficient of carbon relative to graphite
$N_{Ar}$	- Rate of argon flow in $Kmoles/second$

- $N_{CO}$  - Rate of  $CO$  generated in  $\dot{K}moles/second$
- $N_{O_2}$  - Rate of oxygen flow in  $\dot{K}moles/second$
- $W$  - Bath weight in  $\dot{K}g$
- $M$  - Atomic weight of the element indicated by the subscript
- $\beta$  - Factor that takes into account the relative amounts of  
 $Cr$  and  $Fe$ ,  $Mn$  etc oxidized during the process

# Chapter 1

## Introduction

The virgin practice of stainless steelmaking[1], in which the base scrap was melted and refined and the chromium units were added as low carbon ferrochromium, was initially used for a number of years. Since the stainless scrap generated could not be reused efficiently in the virgin practice, stainless scrap continued to accumulate and the price of stainless steel scrap became quite low compared to the inherent value of its alloy content. However, as soon as oxygen became available commercially in large quantities at a reasonable price, oxygen injection processes were developed. For example in duplex processes, electric arc furnace is used only for melting while the refining is carried out in an extra vessel like Argon-Oxygen-Decarburization(AOD), Vacuum-Oxygen-Decarburization(VOD), or Creusot-Loire-Uddeholm(CLU). Although both AOD and VOD are still being used, the AOD process appears to be the dominant one. The main advantage of AOD process is that it allows the use of cheap high carbon ferro-chrome instead of costly low carbon ferro-chrome as a source chromium addition.

The AOD process was first demonstrated on laboratory scale by the Linde division of Union Carbide Corporation[2] and then developed on 15/20 ton pilot plant scale jointly with Joslyn stainless steel division in the year 1967. At the beginning of 1971, there were only four AOD installations[2] out of which three were located in USA and the largest one of 20 tons capacity was located in Europe. Thereafter, the growth of AOD was rapid, and

in early 1977, there were about 44 vessels in operation in 10 countries; the total capacity amounted to about 1526 tons. At present, there are more than 1000 vessels in several countries. In India, Sippy Pramod Steel Alloy Private Limited, Tarapore, Maharashtra were the first to introduce AOD in 1980.

In this chapter, after a brief description of the AOD vessel, AOD practice and the technical developments in AOD, the scope of Thesis will be discussed.

## 1.1 AOD Process

### 1.1.1 AOD Vessel Description

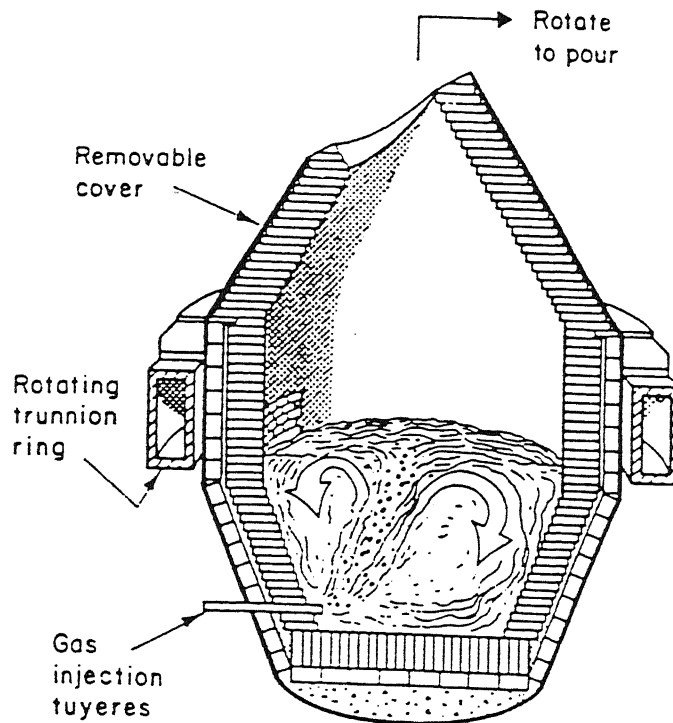


Figure 1.1: Schematic diagram: AOD Converter

Schematic diagram of a AOD vessel is shown in Figure 1.1. For a 80 ton converter, the height of vessel is approximately 6.8 metres and diameter (of cylindrical portion) is 4.4 metres[3]. The free internal volume is  $33 \text{ m}^3$ . The vessel is mounted on trunions and can

be tilted for tapping. The tapping pit is usually equipped with a motorised platform which can be rolled in towards the vessel. No taphole is used and reactor is tapped over the spout. The tuyeres (made of copper) are located on the bottom side through which oxygen-argon mixture or oxygen-air mixture is passed. The vessel is lined with magnesite-chromite bricks to withstand basic slag and high temperatures generated during the process.

### 1.1.2 AOD Practice

The Liquid semiproduct, used as initial feed charge for blowing in AOD converters[3], is melted in electric-arc furnaces from a charge composed of cheap high-carbon ferroalloys. The semiproduct and the slag are poured into the AOD converter. The blowing process is divided into three periods, each period is characterized by a different oxygen-to-argon ratio in the blow mixture. The initial concentration of carbon in the semiproduct is 2.0-2.5% when making ferritic chromium steel and 1.3-1.7% carbon when making austenitic chromium-nickel steel. The melt temperature in the ladle may range from 1640-1660°C. The first blow period is continued for upto 35 minutes and the oxygen-argon are used in 3:1 ratio. Overheating of the metal is prevented by additions of alloy scrap. The temperature of the metal is around 1650°C. The carbon content at the end of first blow is approximately 0.4%. The second blow is continued until the carbon content decreases to 0.18-0.2%. The oxygen-argon ratio in this period is 1:1 and the blow is continued for around 9 minutes. In the third period, the carbon content is reduced to approximately 0.035%. The blow is continued for around 15 minutes and the oxygen-argon ratio is 1:2. The temperature of metal reaches upto 1720°C at the end of this period. A higher temperature is undesirable because it is harmful for the life of converter lining. At the end of the decarburization period, lime and ferro-silicon are charged into the converter from bins in order to reduce and recover chromium from slag. The reducing period lasts for about 5 minutes and the overall yield of chromium is more than 98%. The slag after reduction (containing less than



1% chromium oxide) is skimmed off. Upon addition of new slag-forming materials, the metal is blown intensively with argon only. During this period upto 95% of sulphur passes from the metal to slag and the residual sulphur concentration at the end of process is less than 0.010%. Metal is now tapped into a ladle and sent to the casting bay.

The log sheets for five typical stainless steel heat produced in the AOD at Starwire India Ltd, Ballabgarh, are given in Appendices A-E. The liquid steel semiproduct, used as feed charge in AOD, is obtained from EAF. The AISI-304 stainless steel heat in Appendix B contains 2.09% carbon, 22.15% chromium and 2.15% nickel. The initial temperature of the melt is approximately  $1470^{\circ}\text{C}$ . As discribed above, blowing is done in three stages (but air/nitrogen mixture only).

Stage1: First stage of blow lasts for 22 minutes. The flow rate of oxygen and air used are  $5.0\text{ m}^3/\text{min}$  and  $0.6\text{ m}^3/\text{min}$ , respectively. The melt contains 0.96% carbon and 20.70% chromium after the first stage of blow. The temperature of the melt is  $1870^{\circ}\text{C}$ . This temperature is unusually high because of excessive oxidation of chromium and heat imbalance in charge.

Stage2: Second stage of blow is continued for 32 minutes. The flow rates of oxygen and air used are  $4.9\text{ m}^3/\text{min}$  and  $0.6\text{ m}^3/\text{min}$ , respectively. During the blow 500 k.g of lime and 95 kg of high carbon ferro-manganese are added. The melt contains 0.21% carbon and 18.10% chromium after the second stage of blow and the temperature of melt is  $1725^{\circ}\text{C}$ .

Stage3: Third stage of blow is continued for 21 minutes. The flow rates of oxygen and air used are  $1.7\text{ m}^3/\text{min}$  and  $2.8\text{ m}^3/\text{min}$ , respectively. During this blow, 250 kg of scrap is added (as a coolant) into the melt. The temperature of melt at the end of blow is  $1715^{\circ}\text{C}$  and the carbon and chromium content are 0.08% and 15.95%, respectively.

After the first three stages (of decarburization), alloying additions of nickel and boron are made. Finally, ferro-silicon is added to reduce chromium oxide in slag. During the reduction period,  $2.2\text{ m}^3/\text{min}$  argon and  $0.6\text{ m}^3/\text{min}$  air are blown for good mixing and

reduction. Then, the slag off is done followed by tapping of stainless steel ladle. The ladle is fitted with a porous plug for gentle argon stirring during the time of transportation so as to homogenize the bath for temperature and composition.

### 1.1.3 Technical Developments in AOD Process

Two important technical developments in AOD process are nitrogenation and powdered nickel oxide addition.

#### Nitrogenation

There are two aspects of use of nitrogenation[4]. First, nitrogen improves the mechanical properties of austenitic stainless steels. Second, nitrogen is much cheaper than argon and hence nitrogen can be used to replace argon. As nitrogen bearing alloys are costly, nitrogen can be introduced into the steel by injecting gaseous nitrogen in place of argon in the early stages of the process. Excess nitrogen can be flushed off during the third stage by blowing argon for a short period. In most of the AOD plants, during the first stage and second stages of blow, argon is substituted by nitrogen or air, while maintaining 3:1 and 1:1 ratio, respectively. Most of the austenitic steel grades permit considerable amount of residual nitrogen in their specification (at the end of AOD treatment nitrogen content is about 0.025% only). In contrast with austenitic stainless steels, strict control over nitrogen is necessary in case of ferritic stainless steels. Even in the case of ferritic stainless steels it is apparent that the bulk of argon consumed can be used in the form of cheap crude argon (which has up to 2% oxygen and 0.4% nitrogen as impurities) without any problem.

#### Use of Nickel Oxide (NiO) Addition

Addition of nickel in usual AOD practice was earlier done by adding electrolytic nickel or Ferro-nickel(Fe-Ni), but both of these are costly raw materials. Nowadays, nickel oxide sinter is used[4] in place of nickel. Powdered nickel oxide is blown-in to reduce consumption

of oxygen and lower the temperature of the bath. This method has proved to be successful in that a good yield of nickel is obtained and cost is also lowered.

## 1.2 Scope of Thesis

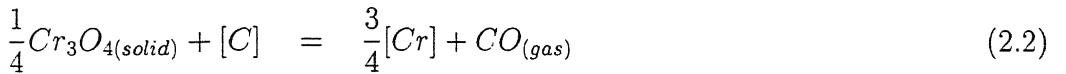
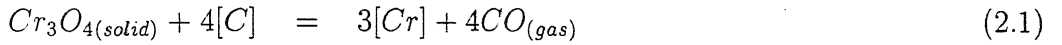
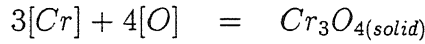
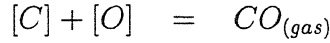
The thermochemical fundamentals of stainless steel refining are discussed in chapter 2 followed by description of static model for AOD process. Heat balance calculations (to calculate the rise in bath temperature) are described in detail. The calculation procedure adopted for static model is explained by means of sample calculations. The kinetic aspects of stainless steel refining are discussed in chapter 3. The calculation procedure adopted in the dynamic model for AOD is described through sample calculations. The static and the dynamic models developed in this work are applied to several heats produced in a steel shop (chapter 4). Importance of the adjustment parameters (like the rate constant, heat loss rate, , etc) is discussed in detail for each heat. Finally, the conclusions of present studies are summarized in chapter 5 alongwith suggestions for further work.

# Chapter 2

## Static Model for Stainless Steelmaking in AOD

### 2.1 Thermochemistry of Stainless Steel Refining

The equilibria between of oxygen, carbon and chromium are represented through following equations



$$\log K = \log \left[ \frac{[Cr]^{3/4} P_{CO}}{f_C [C]} \right] = -\frac{11520}{T} + 7.64 \quad (2.3)$$

$$[C] = \left[ \frac{[Cr]^{3/4} P_{CO}}{K f_C} \right] \quad (2.4)$$

Here, activity of chromium oxide and activity coefficient of chromium are approximately taken as unity. Activity coefficient of carbon is  $f_C$ . Interaction parameters are[5]

$$e_C^{(C)} = 0.14, \quad e_C^{(Cr)} = -0.024, \quad e_C^{(Mn)} = -0.012, \quad e_C^{(Si)} = 0.08.$$

Equations (2.3) and (2.4)[6] show that the carbon content in steel can be reduced as the temperature increases and the partial pressure of carbon monoxide decreases. Figure 2.1[7] is (obtained from Equation 2.4.) shows that if  $P_{CO}$  is one atmosphere, the equilibrium carbon content of a 18% chromium steel is 0.23% carbon at 1700°C. However if  $P_{CO}$  is reduced to 0.1 atmosphere, the carbon content can be reduced to 0.02%. This principle of lowering the partial pressure of carbon monoxide to obtain low carbon content of the bath is the basic principle of stainless steel refining. The three process routes that may be adopted for decarburization of stainless steel are schematically shown in Figure 2.2.[7]

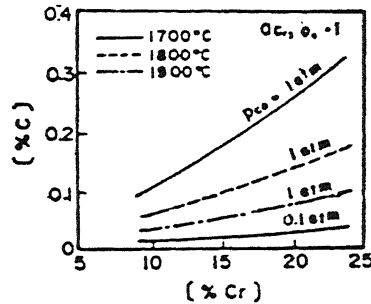


Figure 2.1: Equilibrium relationship between chromium and carbon in steel

Route A: is process at one atmosphere pressure, to achieve a carbon content of 0.06% or lower, in order to get back chromium from slag, ferro-silicon is added to reduce chromium oxide.

Route B: is a process under low  $P_{CO}$  condition (using vacuum or a dilution gas like argon and air).

Route C: is a combined process in which the refining is first carried out at one atmo-

sphere pressure until the carbon content decreases to the point P. Hereafter the steel is treated without oxygen gas under low  $P_{CO}$  condition. The oxygen for decarburization is supplied by the oxides in the slags (viz. chromium oxide) which are formed during the first refining period.

Electric arc furnace process comes under Route A. The duplex process like AOD, VOD, CLU and some other modified processes are classified into Route B. Route C corresponds to VOD-converter process[6].

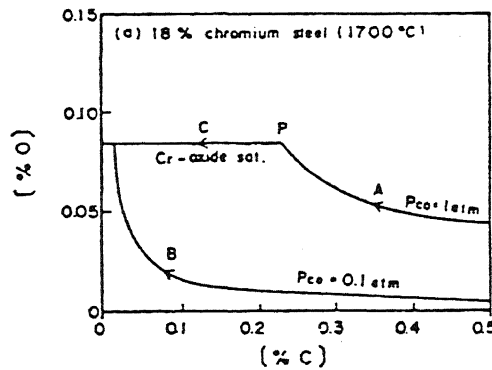


Figure 2.2: Process routes in stainless steel refining

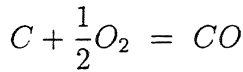
The present work relates to Route B using AOD process.

## 2.2 Static Model for AOD Process

A simple static model of AOD process has been proposed by Semin *et.al*[5]. It is assumed that the oxygen potential of liquid metal remains constant throughout oxygen injection (i.e., in equilibrium with  $Cr_3O_4(solid)$ ). For chromium contents of liquid steel in excess of 9% chromium, decarburization is described by the reaction Equations (2.2) to (2.4).

Suppose during the time  $\Delta t$  (minute) of injection,  $\Delta Q_d$   $m^3/ton$  of diluent gas (say argon) and  $\Delta Q_O$   $m^3/ton$  of oxygen are introduced into the liquid steel. The stoichiometric

amount of carbon oxidized  $\Delta[C]_1\%$ , can be determined from



Thus, the number of moles of carbon reacted is given by  $N_C = \frac{\Delta[C]_1}{100} \times \frac{1000}{12.011}$  ~~k~~ moles/ton.

The corresponding number of moles of  $CO$  formed is given by,  $N_{CO} = \frac{\Delta[C]_1}{100} \times \frac{1000}{12.011}$  ~~k~~ moles/ton,

or  $\frac{\Delta[C]_1}{100} \times \frac{1000}{12.011} \times 22.414$   $m^3/ton$ . The number of moles of  $CO$  formed in  $m^3/ton$  is

$$\Delta Q_{CO} = 18.7\Delta[C]_1 \quad (2.5)$$

Partial pressure of  $CO$  is obtained from

$$P_{CO} = \frac{\Delta Q_{CO}}{\Delta Q_d + \Delta Q_{CO}} P_{total} \quad (2.6)$$

On substituting the value  $\Delta Q_{CO}$  from Equation (2.9)

$$P_{CO} = \frac{18.7\Delta[C]_1}{\Delta Q_d + 18.7\Delta[C]_1} P_{total} \quad (2.7)$$

The equilibrium value of  $P_{CO}$  can be calculated from Equation (2.3). At a temperature  $T_0$  the equilibrium constant,  $K_0$  is given by

$$K_0 = \frac{[Cr]_0^{3/4} P_{CO}}{f_C [C]_0}$$

On substituting for  $P_{CO}$  from Equation (2.7), the amount of carbon oxidized is

$$\Delta[C]_1 = \frac{\Delta Q_d K_0 f_C [C]_0}{18.7 ([Cr]_0^{3/4} P_{total} - K_0 f_C [C]_0)} \% \quad (2.8)$$

where  $[C]_0$  is initial Carbon content,  $[Cr]_0$  is initial Chromium content,  $T_0$  is initial temperature $^\circ K$ ,  $[K]_0$  is equilibrium constant related to the initial temperature  $T_0$  and  $f_C$  is the activity coefficient of carbon.

The relation between oxygen required for the oxidation of  $\Delta[C]_1$  amount of carbon is

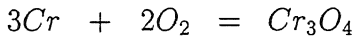
$$\frac{1}{2} \times \text{number of moles of carbon reacted} = \text{number of mole of } O_2 \text{ used}$$

$$= \frac{\Delta[C]_1}{100} \times \frac{1000}{12.011} \times \frac{1}{2} \text{ k moles/ton}$$

$$= \frac{\Delta[C]_1}{100} \times \frac{1000}{12.011} \times \frac{22.414}{2} \text{ m}^3/\text{ton}$$

$$= 9.35 \Delta[C]_1 \text{ m}^3/\text{ton}$$

The balance oxygen is used for the oxidation of chromium, silicon, iron, manganese and other elements in the liquid steel. If it is assumed that almost all the remaining oxygen is used for the oxidation of chromium, then, the amount of chromium oxidized ( $\Delta[Cr]_1\%$ ) can be obtained from



i.e.,  $\frac{2}{3}$  mole of oxygen is required for each mole of chromium,

$$\frac{3/2 \times (\Delta Q_O - 9.35 \Delta[C]_1)}{22.414} \text{ k moles/ton of } O_2 \text{ oxidizes} =$$

$$\frac{\Delta[Cr]_1}{100} \times \frac{1000}{52} \text{ k moles/ton } Cr$$

or

$$\frac{\Delta[Cr]_1}{100} \times \frac{1000}{52} = \frac{3}{2} \times \frac{(\Delta Q_O - 9.35 \Delta[C]_1)}{22.414}$$

The amount of chromium oxidized is thus

$$\Delta[Cr]_1 = \frac{3 \times 52 \times 100}{2 \times 1000 \times 22.414} (\Delta Q_O - 9.35 \Delta[C]_1)$$

$$= \frac{3 \times 52}{2 \times 10 \times 22.414} (\Delta Q_O - 9.35 \Delta[C]_1)$$

$$= 0.348 (\Delta Q_O - 9.35 \Delta[C]_1) \%$$



or

$$= 0.348 \times \beta \times (\Delta Q_O - 9.35 \Delta[C]_1) \% \quad (2.9)$$

where  $\beta$  is the factor that takes into account the relative amounts of  $Cr$  and  $Fe, Mn$  etc oxidized during the process (in above case  $\beta = 1.0$ ).

## 2.3 Heat Balance Calculations

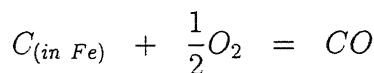
The change in bath temperature due to oxidation of carbon, chromium etc can be determined from the heat balance calculations. Reference temperature is taken as  $298^\circ K$ . The rise in the bath temperature  $\Delta T$  is given by

$$\Delta T = \frac{\Delta H_{\Delta[C]} + \Delta H_{\Delta[Cr]} + \Delta H_{\Delta[Si]} + \Delta H_{\Delta[Fe]} - \Delta H_d}{W C_{p(bath)}} - V_t \Delta t \text{ } ^\circ K \quad (2.10)$$

where  $\Delta H_{\Delta[C]}$  is heat evolved during oxidation of  $\Delta[C]\%$  carbon in  $\text{kJ}$ ,  $\Delta H_{\Delta[Cr]}$  is heat evolved during oxidation of  $\Delta[Cr]\%$  chromium in  $\text{kJ}$ ,  $\Delta H_{\Delta[Si]}$  is heat evolved during oxidation of  $\Delta[Si]\%$  silicon in  $\text{kJ}$ ,  $\Delta H_{\Delta[Fe]}$  is heat evolved during oxidation of  $\Delta[Fe]\%$  iron in  $\text{kJ}$ ,  $\Delta H_d$  is heat consumed in heating diluent gas in  $\text{kJ}$ ,  $W$  is mass of the liquid bath in  $\text{kg}$ ,  $C_{p(bath)}$  is heat capacity of bath in  $\text{kJ/kg.K}$ ,  $V_t$  is parameter characterizing the rate of cooling of the liquid bath as a result of heat losses in  $K/min$  and  $\Delta t$  is small time interval in  $min$ . Method of calculation of each of these terms is explained below.

### 2.3.1 Calculation of $\Delta H_{\Delta[C]}$

The reaction considered is



The steps involved in calculating  $\Delta H_{\Delta[C]}$  are

**Step 1:** Heat of dissolution of carbon: heat evolved as result of bringing out carbon from dissolved state to pure state.



**Step 2:** Sensible heat of carbon: heat evolved as a result of cooling carbon from bath temperature to  $298^\circ K$ .  $\Delta H_2 = 23.154T - 11042.71 \text{ kJ/kmole}$ .

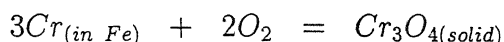
**Step 3:** Heat of oxidation: heat evolved due to the reaction  $C + \frac{1}{2}O_2 = CO$  at  $298^\circ K$ .  $\Delta H_3 = -110530 \text{ kJ/kmole}$ .

**Step 4:** Sensible heat of  $CO$  gas: heat required to raise the temperature of  $CO$  gas from  $298^\circ K$  to bath temperature.  $\Delta H_4 = 34.6T - 12636.37 \text{ kJ/kmole}$ .

**Step 5:** Addition of all the heat values obtained from step 1-4 yields  $\Delta H_{\Delta[C]}$ .

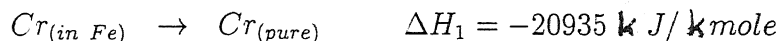
### 2.3.2 Calculation of $\Delta H_{\Delta[Cr]}$

The reaction considered is



The steps involved in calculating  $\Delta H_{\Delta[Cr]}$  are

**Step 1:** Heat of dissolution of chromium: heat evolved as a result of bringing out chromium from dissolved state to pure state.



**Step 2:** Sensible heat of chromium: heat evolved as a result of cooling chromium from bath temperature to  $298^\circ K$ .  $\Delta H_2 = 38.973T - 18138.6 \text{ kJ/kmole}$ .

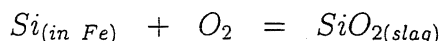
**Step 3:** Heat of oxidation: heat evolved due to the reaction  $3Cr_{(solid)} + 2O_2 = Cr_3O_4(solid)$  at  $298^\circ K$ .  $\Delta H_3 = -1141376.2 \text{ kJ/kmole}$ .

**Step 4:** Sensible heat of  $Cr_3O_4(solid)$ : heat required to raise the temperature of  $Cr_3O_4$  from  $298^\circ K$  to bath temperature.  $\Delta H_4 = 130.47T - 45027 \text{ kJ/kmole}$ .

**Step 5:** Addition of all the heat values obtained from above four step 1-4 yields  $\Delta H_{\Delta[Cr]}$ .

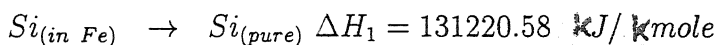
### 2.3.3 Calculation of $\Delta H_{\Delta[Si]}$

The reaction considered is



The steps involved in calculating  $\Delta H_{\Delta[Si]}$  are

**Step 1:** Heat of dissolution of silicon: heat evolved as a result of bringing out silicon from dissolved state to pure state.



**Step 2:** Sensible heat of silicon: heat evolved as result of cooling silicon from bath temperature to  $298^\circ K$ .  $\Delta H_2 = 26.788T + 40734.5 \text{ kJ/kmole}$ .

**Step 3:** Heat of oxidation: heat evolved due to the reaction  $Si_{(solid)} + O_2 = SiO_{2(solid)}$  at  $298^\circ K$ .  $\Delta H_3 = -911509.9 \text{ kJ/kmole}$ .

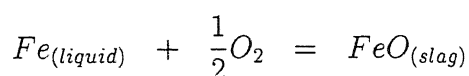
**Step 4:** Sensible heat of  $SiO_2$ : heat required to heat  $SiO_{2(solid)}$  from  $298^\circ K$  to  $SiO_{2(liquid)}$ .  $\Delta H_4 = 72.85T - 27027.67 \text{ kJ/kmole}$ .

**Step 5:** Heat required to dissolve  $SiO_{2(liquid)}$  in slag.

**Step 6:** Addition of all the heat values obtained from step 1-5 yields  $\Delta H_{\Delta[Si]}$ .

### 2.3.4 Calculation of $\Delta H_{\Delta[Fe]}$

The reaction considered is



- Step 1:** Sensible heat of  $Fe$ : heat evolved as a result of cooling iron from bath temperature to  $298^\circ K$ .  $\Delta H_1 = 40.99T - 2183.10 \text{ kJ/kmole}$ .
- Step 2:** Heat of oxidation: heat evolved due to the reaction  $Fe_{(solid)} + \frac{1}{2}O_2 = FeO_{(solid)}$  at  $298^\circ K$ .  $\Delta H_2 = -264001.99 \text{ kJ/kmole}$ .
- Step 3:** Sensible heat of  $FeO$ : heat required to heat  $FeO_{(solid)}$  from  $298^\circ K$  to  $FeO_{(liquid)}$ .  $\Delta H_3 = 94.24T - 51092.99 \text{ kJ/kmole}$ .
- Step 4:** Heat required to dissolve  $FeO_{(liquid)}$  in slag.
- Step 5:** Addition of all the heat values obtained from step 1-4 results  $\Delta H_{\Delta[Fe]}$

### 2.3.5 Calculation of $\Delta H_d$

$$\Delta H_d = m \cdot C_p \cdot (T_{out} - T_{in})$$

where  $m$  is moles of diluent gas entered into the bath in  $\text{kmoles}$ ,  $C_p$  is heat capacity of diluent gas in  $\text{kJ/kmole}^\circ\text{Kelvin}$ ,  $T_{in}$  is incoming temperature of diluent gas in  $^\circ K$ ,  $T_{out}$  is outgoing temperature of diluent gas in  $^\circ K$ .

## 2.4 Calculation Procedure Adopted for Static Model

Steps of the calculations procedure adopted are as follows

- Step 1:** Time interval  $\Delta t$  is small enough to that parameters  $[C]$  and  $K_0$  in Equation (2.8) may be treated as constant. Calculate equilibrium constant at given temperature and activity coefficient of carbon for the known bulk concentration.
- Step 2:** Find out  $\Delta[C]_1$ ,  $\Delta[Cr]_1$ ,  $\Delta T_1$  for time interval  $\Delta t$ .
- Step 3:** Find out new values of bulk concentrations  $[C]_1$ ,  $[Cr]_1$ , bath temperature  $T_1$  and bath weight at the end of time step.
- Step 4:** Go to step 1 and repeat the calculation for the new time step.

As an example, the details of calculations involved in each of the steps is given below.

Suppose the initial values of the variables are

$$[C]_0 = 0.12; \quad [Cr]_0 = 16.70; \quad [Si]_0 = 0.063; \quad [Mn]_0 = 0.8; \quad T_0 = 1998.0^\circ K;$$

$$\Delta t = 0.1 \text{ min}; \quad \Delta Q_d = 0.051 \text{ m}^3/\text{ton}; \quad \Delta Q_o = 0.026 \text{ m}^3/\text{ton}; \quad Mass = 41186 \text{ kg}$$

### Step 1: Calculation of equilibrium constant and activity coefficient of carbon

The equilibrium constant at the initial temperature  $T_0 = 1998.0^\circ K$  is calculated from Equation (2.3)

$$\log K_0 = -\frac{11520}{T} + 7.64 = -\frac{11520}{1998} + 7.64 = 1.874$$

or

$$K_0 = 74.85$$

The activity coefficient of carbon is calculated from

$$\log f_C = e_C^C[wt\%C] + e_C^{Cr}[wt\%Cr] + e_C^{Si}[wt\%Si] + e_C^{Mn}[wt\%Mn]$$

or

$$\log f_C = 0.14 \times 0.12 - 0.024 \times 16.70 + 0.08 \times 0.063 - 0.012 \times 0.8 = -0.38856$$

or

$$f_C = 0.4087$$

### Step 2:

Calculation of  $\Delta[C]\%$

Let the total pressure in vessel be,  $P_{total} = 1.5 \text{ atm}$ , then from Equation (2.12)

$$\Delta[C]_1 = \frac{\Delta Q_d K_0 f_C [C]_0}{18.7 ([Cr]_0^{3/4} P_{total} - K_0 f_C [C]_0)} \%$$

$$\Delta[C]_1 = \frac{0.051 \times 74.85 \times 0.4087 \times 0.12}{18.7 ([16.70]^{3/4} \times 1.5 - 74.85 \times 0.4087 \times 0.12)} \%$$

$$\Delta[C]_1 = \frac{0.1872}{163.092} = 0.0011478 \%$$

**Calculation of  $\Delta[Cr]\%$**

The chromium loss is calculated from Equation (2.9.).

$$\Delta[Cr]_1 = 0.348 \beta (\Delta Q_O - 9.35 \Delta[C]_1) = 0.348 \times 1.0 (0.026 - 9.35 \times 0.0011478) = 0.005313288 \%$$

**Calculation of  $\Delta T$**

The rise in the bath temperature is calculated from heat balance calculations.

$$\text{Amount of carbon oxidized} = 0.0011478 \%$$

$$\text{Hence, heat liberated due to oxidation of } \Delta[C]\% \text{ carbon} = 0.03936 \times (-111870.192) = -4403.21 \text{ KJ.}$$

$$\text{Amount of Chromium oxidized} = 0.005313288 \%$$

$$\text{Hence, heat liberated due to oxidation of } \Delta[Cr]\% \text{ chromium} = 0.04208 \times (-1006393.94) = -42349.057 \text{ KJ.}$$

$$\text{Now, the heat consumed in heating diluent gas} = m_{Ar} \cdot C_p \cdot (T_{out} - T_{in})$$

$$= 0.0859 \times 4.187 \times 4.97 \times (1998 - 298) = 3039 \text{ kJ}.$$

Suppose the heat loss factor is assumed as  $4^\circ\text{K}/\text{min}$  and small time step  $\Delta t$  is  $0.1 \text{ min}$ .

Heat Capacity of bath is  $0.779682 \text{ kJ}/(\text{kg}\cdot\text{K})$  and mass of the liquid metal is  $41186 \text{ kg}$ .

Then the rise in temperature is given by

$$\Delta T = \frac{\Delta H_{\Delta[C]} + \Delta H_{\Delta[Cr]} - \Delta H_d}{W C_{p(bath)}} - V_t \Delta t \text{ K}$$

$$\Delta T = \frac{-4403.21 - 42349.057 + 3039}{41186 \times 0.779682} - 4.0 \times 0.1 \text{ K}$$

$$= 0.961^\circ\text{K}$$

**Step 3:**

**Calculation of  $[C]_1$**

The carbon content at the end of first time step is

$$[C]_1 = [C]_0 - \Delta[C]_1 = 0.12 - 0.0011478 = 0.1188152 \%$$

**Calculation of  $[Cr]_1$**

The final chromium content at the end of first time step is

$$[Cr]_1 = [Cr]_0 - \Delta[Cr]_1 = 16.90 - 0.005313288 = 16.695 \%$$

**Calculation of  $T_1$**

The temperature at the end of first time step is

$$T_1 = T_0 + \Delta T = 1998.0 + 0.961 = 1998.961^\circ\text{K}$$

**Calculation of new bath weight**

Weight loss due to  $\Delta[C]_1\%$  carbon oxidation  $= 0.0011478 \times 0.01 \times 41186 = 0.45913 \text{ kg}$ .

Weight loss due to  $\Delta[Cr]_1\%$  chromium oxidation  $= 0.005313288 \times 0.01 \times 41186 = 2.188331 \text{ kg}$ .

New bath weight = Old bath weight - weight loss due to carbon oxidation - weight loss due to chromium oxidation.

$$= 41186 - 0.45913 - 2.188331 = 41183.35 \text{ kg}.$$

**Step 4:**

The calculated values of  $[C]_1$ ,  $[Cr]_1$ ,  $T_1$  become the initial values for the next time step and we continue this procedure up to the final limit. Changes in carbon, chromium and temperature with time are shown in Figure (2.3), (2.4) and (2.5), respectively.



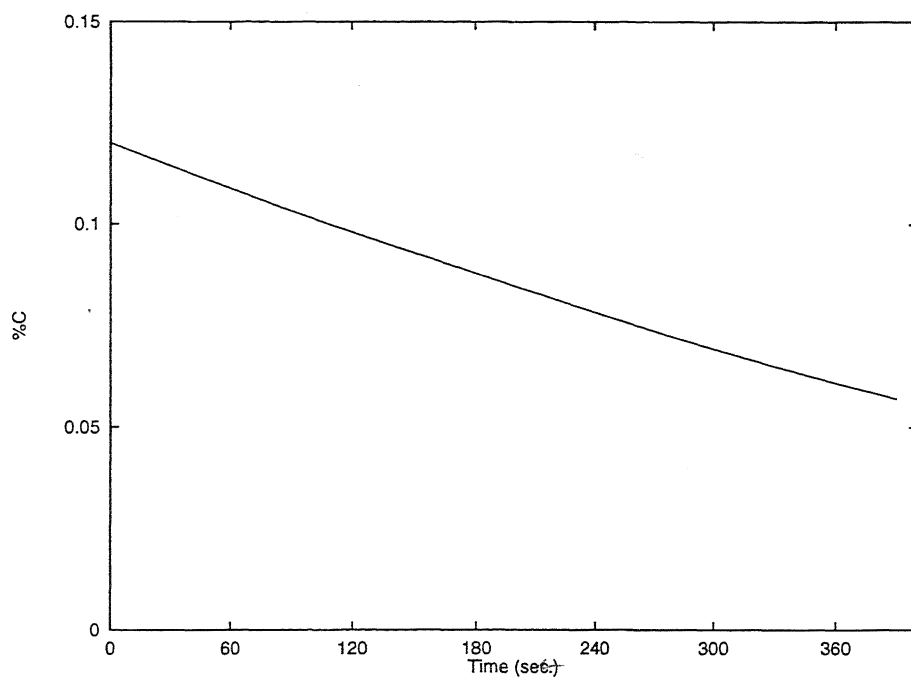


Figure 2.3: Static Model: Carbon versus Time (seconds)

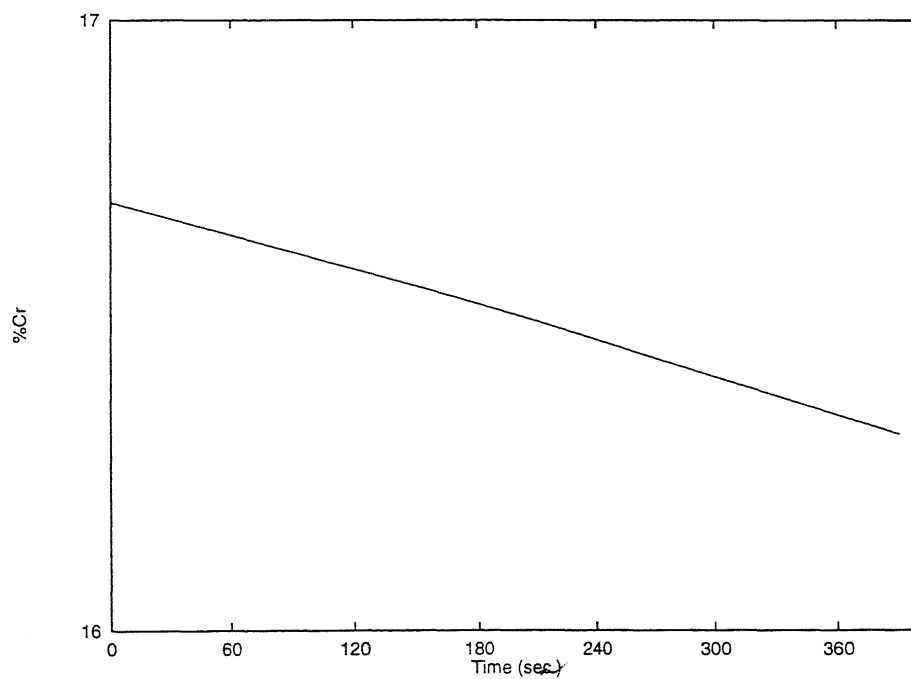


Figure 2.4: Static Model: Chromium versus Time (seconds)

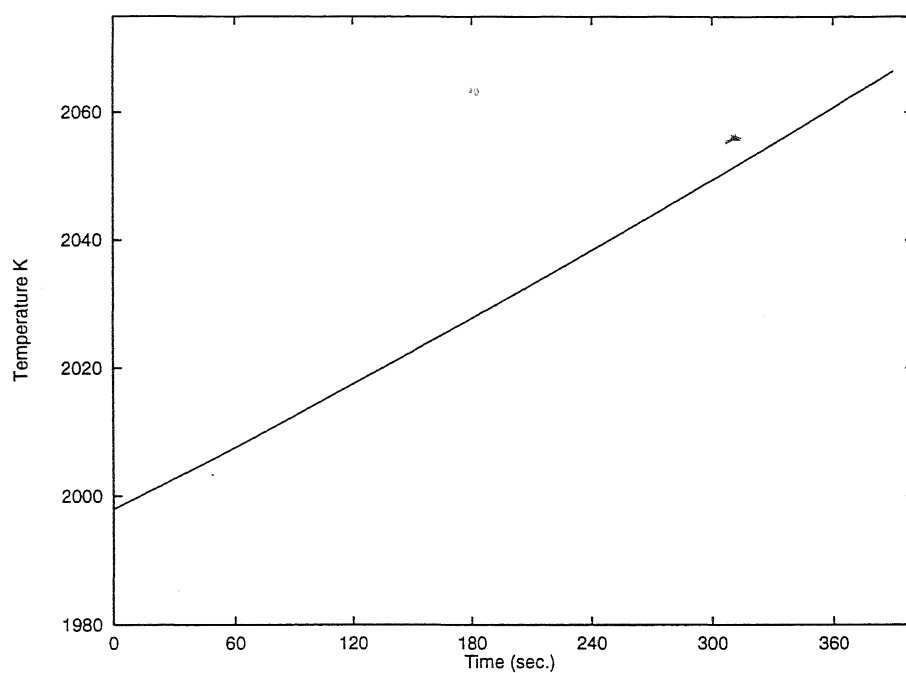


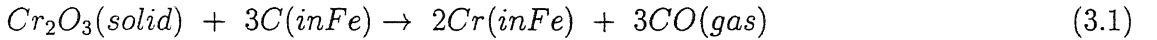
Figure 2.5: Static Model: Temperature(Kelvin) versus Time (seconds)

# Chapter 3

## Dynamic Model for Stainless Steelmaking in AOD

### 3.1 Formulation of Dynamic Model

The main objective in AOD process of stainless steel making is to oxidize carbon in preference to chromium and this is achieved by lowering the partial pressure of  $CO$  gas through inert gas injection ( $Ar$  or  $N_2$ ). Preferential oxidation of carbon also implies that the reaction



moves in forward direction. The effectiveness of argon (or  $N_2$ ) in protecting the chromium from oxidation depends on control of temperature, slag composition, tuyere design and gas flow rate[8]. Fruehan[8] investigated the rate of oxidation of chromium and carbon by  $O_2 - Ar$  mixtures in shallow melts and confirmed that initially chromium is oxidized to  $Cr_2O_3$  at a much faster rate than carbon. As  $Cr_2O_3$  rises with argon bubbles, it is reduced by carbon according to reaction 3.1. Along with chromium, iron is also oxidized to  $FeO$  but it is quickly reduced by chromium. The rate of reduction of chromium by carbon may be controlled by mass transfer of carbon. The average rate of oxidation of carbon can be

represented by

$$\frac{d(\%C)}{dt} = -\sigma[\%C - (\%C)_e] \quad (3.2)$$

where  $\%C$  is the time-dependent average carbon content of the bath,  $(\%C)_e$  is the average carbon content at the bubble surface in local equilibrium with the average chromium content and the average  $CO$  partial pressure in the gas bubbles, and  $\sigma$  is empirical rate parameter which is proportional to average liquid phase mass transfer coefficient. If  $K$  is the equilibrium constant then at low carbon contents the local equilibrium carbon concentration can be obtained from

$$(\%C)_e = \frac{[a_{Cr}]^{2/3}}{K^{1/3}} \frac{10^2 M_C P_{CO}}{M_{Fe} \gamma_C} \quad (3.3)$$

where  $a_{Cr}$  is the average activity of chromium in the melt relative to pure solid chromium,  $M$  is the atomic weight of the element indicated by the subscript,  $\gamma_C$  is the activity coefficient of carbon relative to graphite and  $P_{CO}$  is the average coefficient of carbon relative to bubbles. If the average total pressure in the bath is  $P_{total}$ , the average value of  $P_{CO}$  is given by

$$P_{CO} = \frac{N_{CO}}{N_{CO} + N_{Ar}} P_{total} \quad (3.4)$$

where  $N_{Ar}$  is the rate of argon flow moles/unit time and  $N_{CO}$  is the amount of  $CO$  generated per unit time. If bath weight is  $W$  then  $N_{CO}$  can be related to decarburization rate by

$$N_{CO} = -\frac{d(\%C)}{dt} \frac{10^2 W}{M_C} \quad (3.5)$$

It should be noted that even if the rate oxidation by  $Cr_2O_3$  is controlled by first order chemical reaction Equations 3.2 through 3.5 would still be equally valid. In this case, however the rate parameter  $\sigma$  will represent an average rate constant for the reaction. The value of  $\sigma$  is to be evaluated on the basis of the operating data for given a AOD converter.

The Equation 3.2 is based on the inherent assumption that there is always sufficient oxygen available in the form of chromic oxide to oxidize all the carbon that is transported to the bubble surface. At high carbon levels the driving force for mass transfer of carbon to the bubble surface is sufficiently high and hence, at the oxygen blow rates usually employed in AOD practice, there is insufficient oxygen to oxidize the carbon that is transported to the bubble surface. Thus, at high carbon levels the rate of decarburization, (via the chromic oxide), is determined primarily by the rate of oxygen blow  $N_{O_2}$ , and the rate of decarburization is given by

$$\frac{d(\%C)}{dt} = - \frac{2 M_C N_{O_2}}{10^{-2} W} \quad (3.6)$$

Whether the rate of decarburization is governed by Equation 3.2 or 3.6 will depend on oxygen supply rate and carbon content.

As in other pneumatic steelmaking processes, in AOD also steelmaking most of the silicon is believed to be oxidized in the early stages of the blow. Therefore, in formulating a material balance for the oxidation of chromium and carbon, the time of blow is corrected for the amount of silicon oxidized ( $\Delta\%Si$ ). That is, the time of blow,  $t$  in the preceding and subsequent equations, is the difference  $t = t(actual) - t(Si)$ , represented by

$$t = t(actual) - \frac{10^{-2} W \Delta\%Si}{M_{Si} N_{O_2}} \quad (3.7)$$

where  $\Delta\%Si$  is the amount of silicon oxidized.

The chromic oxide that is not reduced by carbon accumulates in the slag layer. Therefore, the net amount of chromium oxidized to  $Cr_2O_3$ ,  $\Delta\%Cr$  is represented by

$$\Delta\%Cr = \frac{4 M_{Cr} \beta}{3 W \times 10^{-2}} [N_{O_2} \Delta t - \frac{10^{-2} W}{2 M_C} (\%C_{m-1} - \%C_m)] \quad (3.8)$$

where  $\beta$  is the factor that takes into account the relative amounts of  $Cr$  and  $Fe, Mn$  etc. oxidized during the process.

In the present work, the oxide phase considered is  $Cr_2O_3$ . Some investigators believe that  $Cr_3O_4$  is formed. Even if  $Cr_3O_4$  is considered, simple corrections can be made in Equation 3.8 for the oxidation of  $Cr$  to  $Cr_3O_4$ .

## 3.2 Solution Techniques Developed for Dynamic Model

Three solution techniques have been developed in the present work. Let the initial carbon content be 0.2%, the initial chromium content be 10%, average bath temperature be  $1700^\circ C$ , the total gas flow rate be  $0.85 m^3 N/s$  and the initial bath weight be 76000 kg.

The oxygen to argon ratios are usually varied from 3:1 to 1:2 used for stainless steel AISI-409. The equilibrium constant( $K$ ) and the activity coefficient( $\gamma_C$ ) are

$$\log K = -\frac{40970}{T} + 27.31$$

at  $1973^\circ K$ ,  $K = 3504838.56$

$$\log \gamma_C = -0.024[\%Cr] + 0.22[\%C] - 0.25$$

for  $\%Cr = 10\%$ ,  $\%C = 0.2\%$ ,  $\gamma_C = 0.358$

The rate parameter( $\sigma$ ) is relatively independent of temperature and gas composition and is approximately proportional to the total gas flow rate. For the experiments reported in [8] rate parameter of  $0.09 min^{-1}$  has been suggested. For sample calculations, we take  $O_2 - Ar$  ratio as 1:1.

### 3.2.1 Solution Technique - I: Recursive Procedure

A simple solution technique has been developed by assuming a mass transport control of carbon in metal phase as the rate controlling step. The rate equation for the average rate of oxidation of carbon is represented by

$$\frac{d(\%C)}{dt} = -\sigma[\%C - (\%C)_e]$$

Now from Equation (3.3)

$$(\%C)_e = \frac{[a_{Cr}]^{2/3} 10^2 M_C P_{CO}}{K^{1/3} M_{Fe} \gamma_C}$$

and from Equation (3.4) and (3.5)

$$P_{CO} = \frac{N_{CO}}{N_{CO} + N_{Ar}} P_{total} \text{ and } N_{CO} = -\frac{d(\%C)}{dt} \frac{10^{-2} W}{M_C}$$

Steps followed for the solution are as follows

**Step 1:** First we discretize the Equation (3.2) by substituting the forward difference for  $\frac{d(\%C)}{dt}$ .

$$\frac{\Delta C}{\Delta t} = \frac{C_{m+1} - C_m}{\Delta t} = -\sigma [C_m - (\%C)_e]$$

On rearranging the above equation

$$C_{m+1} = C_m - \sigma \Delta t [C_m - (\%C)_e]$$

**Step 2:** Take a small time step  $\Delta t$ . At  $t = 0$ , to start with  $(\%C)_e$  is assumed to be zero. Then, using expression  $C_1 = C_0 - \sigma \Delta t C_0$ , we calculate  $C_1$ .

Let the time step be 0.1 *second* then,  
 $C_1 = 0.2 - (0.0015 \times 0.1 \times 0.2) = 0.19997$ .

$$\Delta C = 0.19997 - 0.2 = -0.000029996, \quad \Delta t = 0.1 \text{ second}.$$

**Step 3** Calculate  $\Delta \%Cr$  using Equation 3.8.

$$\begin{aligned} \Delta \%Cr &= \frac{4 \times 51.9 \times 0.9}{3 \times 76000 \times 10^{-2}} \left[ 0.019 \times 0.1 - \frac{10^{-2} \times 76000}{2 \times 12.011} (0.2 - 0.19997) \right]. \\ \Delta \%Cr &= 0.000078076. \end{aligned}$$

**Step 4:** Calculate  $\frac{\Delta C}{\Delta t}$  and  $N_{CO} = -\frac{\Delta C}{\Delta t} \frac{10^{-2} W}{M_C}$ .

$$\begin{aligned} \frac{\Delta C}{\Delta t} &= -0.00029996. \\ N_{CO} &= \frac{0.00029996 \times 10^{-2} \times 76000}{12.011} = 0.0189801 \text{ kmoles/sec.} \end{aligned}$$

**Step 5:** Calculate  $P_{CO} = \frac{N_{CO}}{N_{CO} + N_{Ar}} P_{Total}$ ,  $P_{Total} = 1.6 \text{ atm}$

$$P_{CO} = \frac{0.0189801}{0.0189801 + 0.019} \times 1.6 = 0.799581 \text{ atm.}$$

**Step 6:** Calculate new bath weight.

New bath weight = Old weight - weight loss due to carbon oxidation -  
weight loss due to chromium oxidation.

$$\text{New bath weight} = 76000 - 0.022797 - 0.059338 = 75999.9 \text{ kg.}$$

**Step 7:** Calculate  $(\%C)_e = \frac{[a_{Cr}]^{2/3} 10^2 M_C P_{CO}}{K^{1/3} M_{Fe} \gamma_C}$ .

$$a_{Cr} = 0.1166 \text{ corresponding to } \%Cr = 10\%$$

$$(\%C)_e = \frac{0.238674 \times 10^2 \times 12.011 \times 0.799581}{144.458 \times 55.847 \times 0.358092} = 0.0793436.$$

**Step 8:** Using step-1 we evaluate  $C_2$

**Step 9:** Repeat steps 3 to 8 and recursively evaluate  $C_m$  till the end of the blow.  
i.e.,  $m\Delta t = \text{End of the blow.}$

The plots of carbon and cumulative chromium loss for various  $O_2 - Ar$  ratios are shown in Figures 3.1 and 3.2.

### 3.2.2 Solution Technique - II: Solution of Quadratic Equation at each time step

Fruehan[8] substituted Equations (3.3), (3.4) and (3.5) to Equation (3.2) and obtained the rate equation for decarburization as follows

$$\frac{d(\%C)}{dt} = -\sigma \left[ \%C + \frac{\left( \frac{[a_{Cr}]^{2/3} W P_{total}}{K^{1/3} M_{Fe} \gamma_C} \frac{d(\%C)}{dt} \right)}{\left( N_{Ar} - \frac{10^{-2} W}{M_C} \frac{d[\%C]}{dt} \right)} \right] \quad (3.9)$$

Let us denote

$$C' = \frac{d(\%C)}{dt}; \quad C = \%C; \quad N = N_{Ar}; \quad Y = \frac{[a_{Cr}]^{2/3} W P_{total}}{K^{1/3} M_{Fe} \gamma_C}; \quad Z = \frac{10^{-2} W}{M_C};$$



On substituting this in Equation 3.9 and simplifying, we get

$$\text{or } Z(C')^2 + (\sigma ZC - N - \sigma Y)C' - \sigma NC = 0 \quad (3.10)$$

The above equation is a quadratic equation in  $C'$  and of the form

$$ax^2 + bx + c = 0$$

where

$$\begin{aligned} C' &= x; \quad a = Z; \quad b = (ZC - N - \sigma Y); \quad \text{and } c = -(\sigma NC); \\ a &= 63.2753Z; \quad b = -0.0150866; \quad \text{and } c = -5.7 \times 10^{-6}; \end{aligned}$$

Solving the quadratic Equation (3.10), we get two roots of  $C'$

$$\begin{aligned} \text{Root1} &= \frac{-b + \sqrt{b^2 - 4ac}}{2a} = 0.00044216 \\ \text{Root2} &= \frac{-b - \sqrt{b^2 - 4ac}}{2a} = -0.000203733 \end{aligned}$$

In the following procedure, by  $C_m$  we mean  $C$  at  $t_m$ .

Steps followed for solution are as follows

**Step 1:** The discretization for  $C'$  is given by

$$C' = \frac{C_m - C_{m-1}}{\Delta t}$$

and hence we have,

$$C_m = C_{m-1} + \text{Root} * \Delta t$$

**Step 2:** Since, carbon content decreases with time, we take the negative root and calculate  $C_1$  using the expression

$$C_1 = C_0 + \text{Root} * \Delta t$$

$$C_1 = 0.2 + (-0.000203733 * 0.1) = 0.19998$$

**Step 3:** Using this  $C_1$  evaluate the coefficients  $a, b$  and  $c$ . Using the Step-1 and Step-2 we evaluate  $C_2$ .

**Step 4:** We repeat steps 1 to 3 and recursively evaluate  $C_m$  till the end of the blow.

Apart from calculating carbon content with respect to time, we calculate chromium loss ( $\Delta\%Cr$ ) at each time step from Equation 3.8. The results match exactly with values shown in Figures 3.1 and 3.2.

### 3.2.3 Solution Technique - III: Quasilinearization Procedure

A quasilinearization[9] technique has been applied in the present work to obtain the solution of Equation (3.10) and the procedure is as follows. It is assumed that the Equation (3.10) is a non-linear ordinary differential equation of the form

$$f(C', C) = 0$$

where

$$f(C', C) = Z(C')^2 + (\sigma ZC - N - \sigma Y)C' - \sigma NC = 0 \quad (3.11)$$

Also, we have the initial condition  $C = C_0$  at  $t = 0$ . In order to solve Equation 3.11, we use an iterative method wherein we linearize Equation 3.11 (using the quasilinearization technique) and solve the linearized problem iteratively. That is

$$\begin{aligned} f(C'_n, C_n) = f(C'_{n-1}, C_{n-1}) &+ (C'_n - C'_{n-1})f_{C'}(C'_{n-1}, C_{n-1}) \\ &+ (C_n - C_{n-1})f_C(C'_{n-1}, C_{n-1}) = 0 \end{aligned} \quad (3.12)$$

Here  $f_{C'}$  is the partial derivative of  $f$  with respect to  $C'$  and  $f_C$  is the partial derivative of  $f$  with respect to  $C$ .

Now, we have to solve Equation (3.12) for  $C_n$ . Keeping  $C_n$  terms on one side and  $C_{n-1}$  terms on the other we get

$$\begin{aligned}
& C'_n f_{C'}(C'_{n-1}, C_{n-1}) + C_n f_C(C'_{n-1}, C_{n-1}) \\
&= C'_{n-1} f_{C'}(C'_{n-1}, C_{n-1}) + C_{n-1} f_C(C'_{n-1}, C_{n-1}) - f(C'_{n-1}, C_{n-1}) \quad (3.13)
\end{aligned}$$

Let

$$A = f_{C'}(C'_{n-1}, C_{n-1})$$

$$B = f_C(C'_{n-1}, C_{n-1})$$

$$D = C'_{n-1} f_{C'}(C'_{n-1}, C_{n-1}) + C_{n-1} f_C(C'_{n-1}, C_{n-1}) - f(C'_{n-1}, C_{n-1})$$

Equation 3.13 becomes,

$$AC'_n + BC_n = D$$

$$C'_n + \frac{B}{A}C_n = \frac{D}{A}$$

$$C'_n + PC_n = Q \quad (3.14)$$

with the initial condition  $C_n = C_0$  at  $t = 0$ . This equation can now be solved iteratively by finite difference method as follows. Discretize the time interval as  $t_0 = 0$ ,  $t_1 = \Delta t$ ,  $t_2 = 2\Delta t$ , ...,  $t_m = m\Delta t$ . Using the forward difference scheme, Equation 3.14 can be written as

$$\frac{C_n(t_m) - C_n(t_{m-1})}{t_m - t_{m-1}} + P(t_m)C_n(t_m) = Q(t_m) \quad (3.15)$$

Simplifying this we get

$$C_n(t_m) = \frac{1}{[1 + (t_m - t_{m-1})P(t_m)]} \{(t_m - t_{m-1})Q(t_m) + C_n(t_{m-1})\} \quad (3.16)$$

## Steps of Solution

- Step 1:** Define a time interval  $t = 0$  to  $t = t_M$  and we know the initial value  $C_n(t_0)$  for  $n=1,2,3,\dots$  etc. i.e., initial carbon content of the bath.
- Step 2:** Give approximate (guess) values  $C_0(t_m)$  for  $m = 1$  to  $m = M$  i.e.,  $C_0(t_m) = C_0(t_0), C_0(t_1), C_0(t_2), \dots, C_0(t_M)$ .
- Step 3:** Find  $C'_0(t_m) \simeq \frac{C_0(t_m) - C_0(t_{m-1})}{(t_m - t_{m-1})}$
- Step 4:** Evaluate  $P(t_m), Q(t_m)$  for  $m = 1, 2, \dots, M$ .
- Step 5:** Using Equation 3.16, we evaluate set of values  $C_1(t_m)$  i.e.,  $C_1(t_1), C_1(t_2), \dots, C_1(t_M)$
- Step 6:** Calculate the sum of the absolute differences between  $C_1(t_m)$  values and  $C_0(t_m)$  values and call it as residue. i.e.,

$$\text{Residue} = \sum_{m=1}^M |C_1(t_m) - C_0(t_m)|$$

If residue is less than certain tolerable value then we stop the procedure. Otherwise we go to step 7.

- Step 7:** Using values of  $C_1(t_m)$  for  $m = 0, 1, 2, \dots, M$ . We can evaluate  $C_2(t_m)$  using the steps 3 to 7. Note that in this procedure we use  $C_1$  in place of  $C_0$ .

Apart from calculating carbon content with respect to time, we calculate chromium loss ( $\Delta\%Cr$ ) from Equation 3.8. The results match exactly with values shown in Figures 3.1 and 3.2

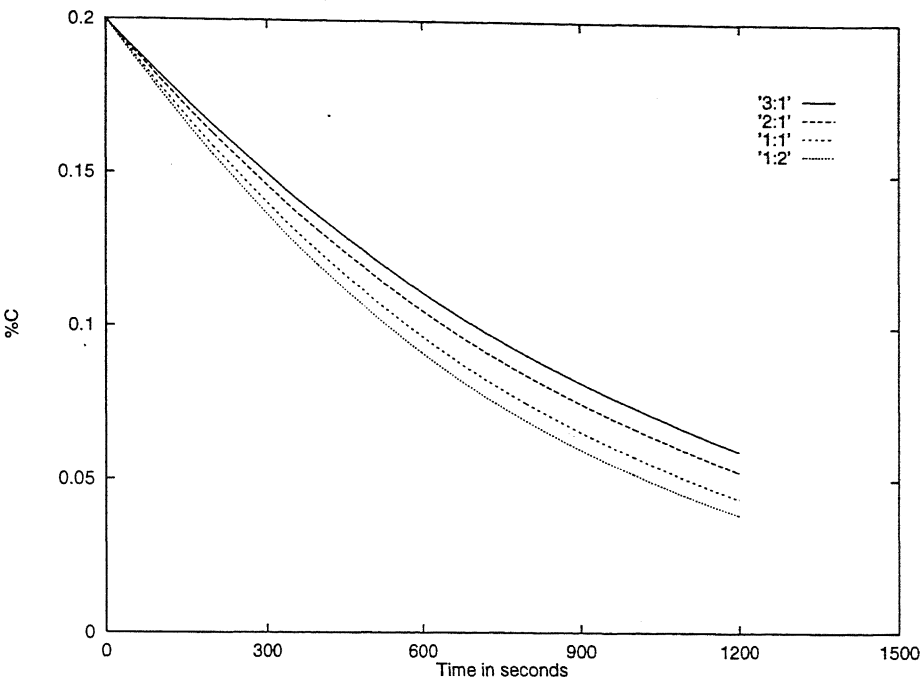


Figure 3.1: Dynamic Model: Carbon versus Time (seconds) at different argon-oxygen ratios, 3:1, 2:1, 1:1, 1:2

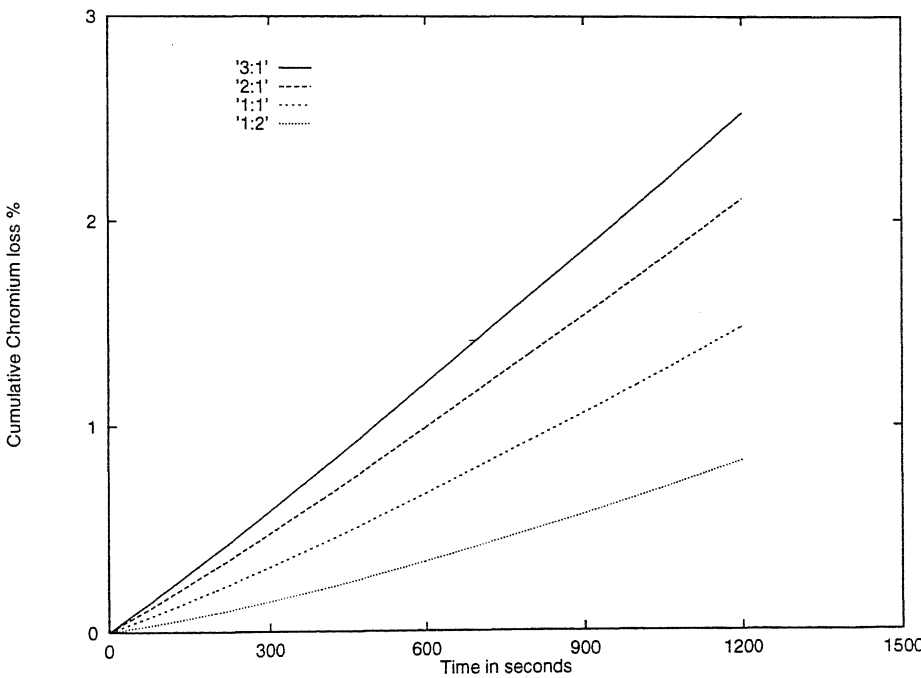


Figure 3.2: Dynamic Model: Cumulative Chromium loss versus Time (seconds) at different argon-oxygen ratios, 3:1, 2:1, 1:1, 1:2

## Chapter 4

# Validation of Static and Dynamic Models

### 4.1 Comparison of Prediction from Static and Dynamic Models on Sample Data

The static and dynamic models developed in chapter 2 and 3, respectively, can be tested on the same set of data to compare their performances. Let the initial conditions for 42 tons converter be: carbon 0.12%, chromium 16.70% and temperature  $1998^{\circ}K$ . The flow rate of oxygen and argon used are  $21.1\text{ m}^3/\text{min}$  and  $10.5\text{ m}^3/\text{min}$ , respectively. The blow is continued for 6.5 minutes. The heat loss factor assumed is  $4\text{ K}/\text{min}$ . The rate parameter (assumed) for dynamic model is  $0.12\text{min}^{-1}$ . The experimental carbon and chromium contents after the blow are 0.047% and 16.45%, respectively. The temperature after the blow is  $2003^{\circ}K$ . The static model predicts: carbon 0.057%, chromium 16.32% and temperature  $2066^{\circ}K$ . The dynamic model predicts: carbon 0.0771%, chromium 16.39% and temperature as  $2063^{\circ}K$ .

The changes in carbon, chromium and temperature as predicted by static model and dynamic model (using solution technique in chapter 3) are plotted in Figures (4.1), (4.2) and (4.3). It can be seen that the results of static and dynamic models differ slightly due to the fact that the equations used to calculate rates of chromium and carbon oxidation

by the two models are not the same. It appears that in a practical situation, as shown in the next section, both static and dynamic models can be used with almost equal degree of success.

## 4.2 Validation of Static and Dynamic Models on Actual AOD Data

Starwire(India) Ltd at Ballabgarh has AOD converter of 8 ton capacity. Details of a typical heat made in the AOD at starwire have already been described in section 1.1.2. Altogether 5 heats ( see Appendix A - E) were closely monitored at Starwire Ltd to record the various measurements. In the following sections, the data are tested by applying both static and dynamic models developed in this work. It may<sup>be</sup> noted that at Starwire India Ltd, air is used instead of argon. The amount of oxygen present in air is therefore added to oxygen to calculate the total oxygen flow rate. The rise in bath temperature is calculated at each time step using the heat balance calculations described in section 2.3. The heat loss factor is calculated (both for static model and dynamic model) by trial and error. In case of dynamic model the average value of rate parameter for oxidation of carbon is found to be  $0.12 \text{ min}^{-1}$  in the carbon range of 2.0% to 0.15% and a slightly lower value of  $0.09 \text{ min}^{-1}$  is used for carbon contents less than 0.15%. The additions of ferroalloys (ferrochrome, ferromanganese, lime, ferro-molibdenum, aluminium , etc) are made during the blow. The corresponding heat consumed by these additions is calculated by assuming a linear dissolution rate over period of 10 minutes; for obtaining more accurate results, however, dissolution models must be developed and incorporated in the dynamic model. In high carbon ranges, from 2.0 - 0.15%, a reliable prediction of chromium is obtained by considering that 80% of oxygen (left after decarburization) is used up for oxidation of chromium (i.e.,  $\beta = 0.8$  in Equations (2.9) and (3.8)) and balance oxygen is utilized for oxidation of iron, manganese, nickel, etc. in the bath. Approximate analysis of ferroalloys

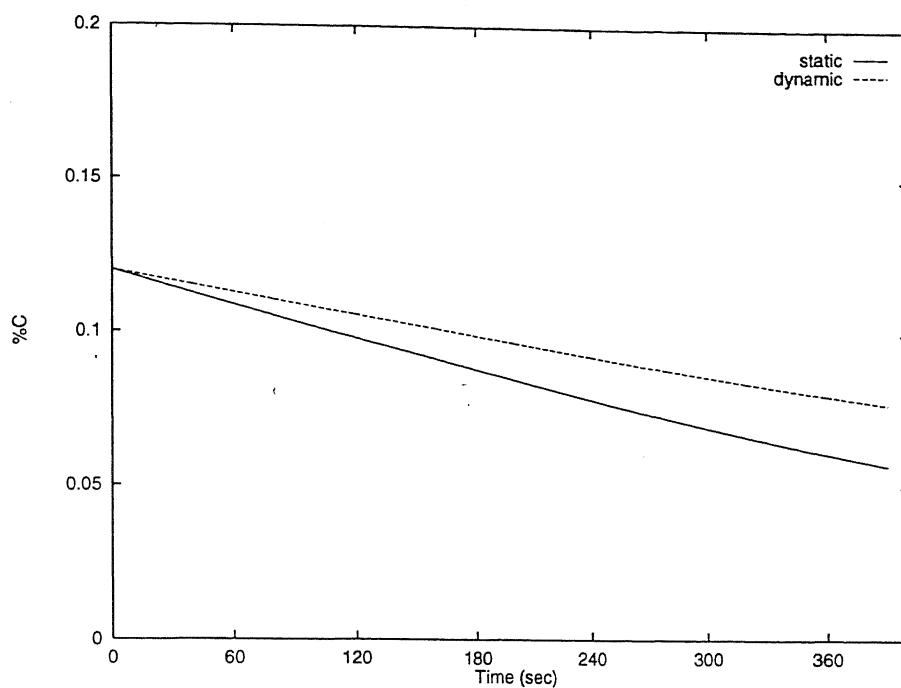


Figure 4.1: Comparison of Static and Dynamic Models: Carbon versus Time (seconds)

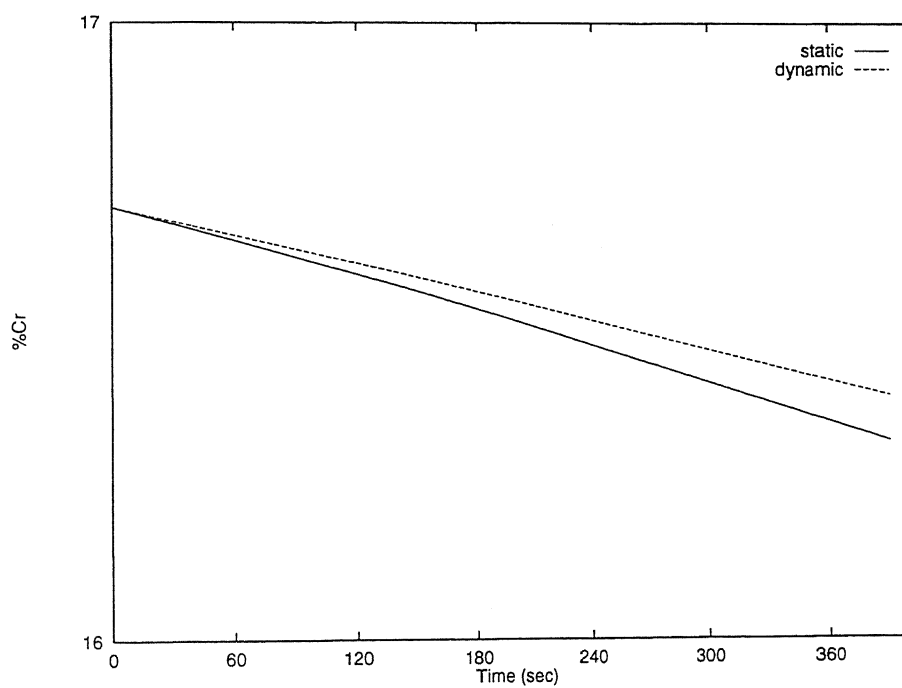


Figure 4.2: Comparison of Static and Dynamic Models: Chromium versus Time (seconds)



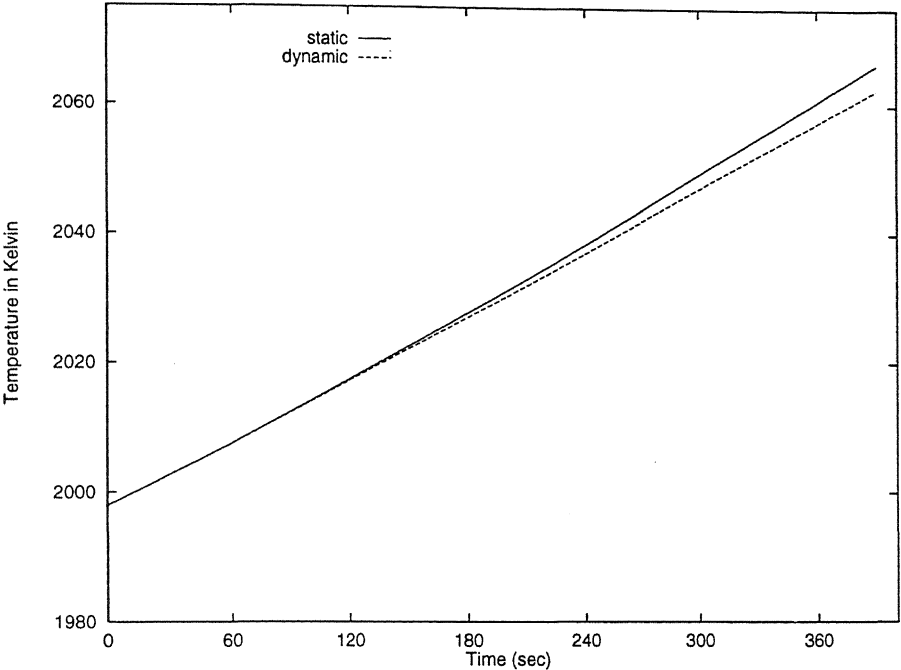


Figure 4.3: Comparison of Static and Dynamic Models: Temperature(Kelvin) versus Time (seconds)

is given in Appendix F. The result obtained for each heat (Tables 1 - 10) are discussed below.

### Heat No 1:AISI - 321:(Log sheet in Appendix A)

**Stage 1:** The initial weight of melt is 8610 ~~kg~~. In stage 1, the blow lasts for 25 minutes. The flow rates of oxygen and air used are  $5.0 \text{ m}^3/\text{min}$  and  $0.8 \text{ m}^3/\text{min}$ , respectively. The initial composition and temperature for the first stage are not given. So we assumed carbon and chromium contents as 1.8% and 19.80%, respectively, and temperature as  $1743^\circ\text{K}$ . The experimental carbon and chromium contents (as reported in logsheets) after the blow are 0.75% and 18.28%, respectively. At the end of stage 1, static model predicts (Table 2) carbon content as 0.757%, chromium content 18.28% and temperature  $1881^\circ\text{K}$ . The average heat loss rate for this blow (found by trial and error) is found to be  $15 \text{ K}/\text{min}$ .

The dynamic model predicts (Table 1) carbon 0.796%, chromium 19.04% and temperature  $1867^\circ\text{K}$ . The average rate parameter for oxidation of carbon is assumed to be  $0.12\text{min}^{-1}$ . The average heat loss rate for this blow (found by trial and error) is found to be  $12.0\text{K}/\text{min}$ .

**Stage 2:** The second stage of blow is continued for 34 minutes. The flow rates of oxygen and air used are  $5.0 \text{ m}^3/\text{min}$  and  $0.8 \text{ m}^3/\text{min}$ , respectively. The initial composition of carbon and chromium are 0.75% and 18.28%, respectively. Initial temperature is assumed as  $1874^\circ\text{K}$ . During this blow, 250~~kg~~ of high carbon ferro chrome, 100~~kg~~ of high carbon ferromanganse, 200~~kg~~ of lime are added 26 minutes after the blow has been started. The experimental carbon and chromium contents after the blow are 0.18% and 15.54%, respectively. The temperature of bath after the blow is  $1996^\circ\text{K}$ .

The static model predicts (Table 2) carbon content as 0.226%, chromium as 15.14% and temperature  $2023^\circ\text{K}$ . The average heat loss factor for this blow is found to be  $24 \text{ K}/\text{min}$ .

The dynamic model predicts (Table 1) the carbon content as 0.188% and chromium

14.67% and temperature as  $1991^{\circ}K$ . The average heat loss factor was found to be  $21\ K/min$ . In this region both static and dynamic model predictions agree closely with experimental values.

**Stage 3:** The third stage of blow is continued for 22 minutes with the flow rate of  $1.8\ m^3/min$  oxygen and  $3.3\ m^3/min$  air. The initial carbon and chromium contents are 0.18% and 15.54%, respectively. The temperature of bath is  $1996^{\circ}K$ . During this blow 250Kg of nickel and 100 kg of lime are added after 9 minutes the blow has been started. The experimental values at the end of stage 3 are carbon 0.055% and chromium 13.03%. The experimental temperature after the blow is  $1995^{\circ}K$ .

The static model predicts (Table 2) carbon content as 0.048%, chromium content 13.73% and temperature  $1955^{\circ}K$ . The average heat loss rate is found to be  $19.5\ K/min$

The dynamic model predicts (Table 1) carbon content as 0.061%, chromium as 13.62% and temperature as  $2025^{\circ}K$ . The average heat loss rate is found to be  $13.5\ K/min$ . In this region, predictions of both the models agree with the experimental values.

### Heat No 2: AISI - 304 (Logsheet in Appendix B)

**Stage 1:** The initial carbon and chromium contents are 2.07% and 22.15%, respectively. The melt contains 0.47% silicon. Oxidation of silicon contributes to rise in temperature of the bath. Since the initial temperature of the bath is not given, calculations for this initial stage are not reported. Initial bath weight is assumed to be 8610 kg. The approximate weight of the bath after this blow is estimated to be 8320 kg.

**Stage 2:** In this stage, the starting compositions of metal is carbon 0.96%, chromium 20.70% and initial temperature is assumed to be  $1880^{\circ}K$ . The bath weight is taken as 8320 Kg. The blow is continued for 32 minutes. The flow rate of oxygen and air used are  $4.9\ m^3/min$  and  $0.6\ m^3/min$ , respectively. During this blow, 95 kg of high carbon ferro-manganese and 500 kg of lime are added. It is assumed that additions are made 10 minutes after the blow (as advised by the operator) has been started. The experimental

carbon and chromium content are 0.21% and 18.10%, respectively. The temperature of the bath after the blow is 1998°K.

The static model predicts (Table 4) carbon content as 0.255%, chromium content 17.36% and temperature 2043°K. The heat loss rate is found to be 19.5 K/min.

The dynamic model predicts (Table 3) carbon content as 0.27%, chromium content 17.25% and temperature 2046°K. The heat loss rate is found to be 14.5 K/min.

Stage 3: The starting compositions is carbon 0.21%, chromium 18.10% and temperature 1998°K. The blow is continued for 21 minutes. The flow rate of oxygen and air used are 1.7 m<sup>3</sup>/min and 2.8 m<sup>3</sup>/min, respectively. During this blow 250 kg of scrap is added as a coolant. The scrap is added after the blow has been started. The experimental carbon and chromium content after the blow are 0.08% and 15.95%, respectively, and the temperature after blow is 1988°K.

The static model predicts (Table 4) carbon content as 0.086%, chromium content 16.59% and temperature 2005°K. The heat loss rate is found to be 15 K/min.

The dynamic model predicts (Table 3) carbon content as 0.087% and chromium content as 16.58% and temperature as 2063°K. The heat loss rate is found to be 9 K/min.

### Heat No 3: AISI - 316 (Logsheet in Appendix C)

Stage 1: The initial weight of bath is 8520 kg. The blow is continued for 50 minutes. The flow rates of oxygen and air used are 5.0 m<sup>3</sup>/min and 1.25 m<sup>3</sup>/min, respectively. The initial carbon and chromium contents are 1.29% and 14.50%, respectively, and the initial temperature is 1796°K. During this blow, 400 kg of high carbon ferro-chrome and 200 kg of lime are added 20 minutes after the blow and 10 minutes after this the additions made are 340 kg of high carbon ferro-chrome and 200 kg of lime. The experimental carbon and chromium contents after the blow are 0.17% and 15.45%, respectively, and temperature of bath after the blow is 1965°K.

An initial temperature of 1743°K is assumed for calculation in static model. The

static model predicts (Table 6) carbon content as 0.205%, chromium content 13.92% and temperature  $2003^{\circ}K$ . The heat loss rate is found to be  $15\text{ K/min}$ .

The dynamic model predicts (Table 5) carbon content as 0.14%, chromium content 9.33% and temperature  $2024^{\circ}K$ . The heat loss rate is found to be  $15\text{ K/min}$ .

Stage 2: The initial carbon and chromium contents are 0.17% and 15.45%, respectively. The initial temperature is  $1964^{\circ}K$ . The blow is continued for 20 minutes. The flow rate of oxygen and air used are  $3.0\text{ m}^3/\text{min}$  and  $2.5\text{ m}^3/\text{min}$ , respectively. The experimental carbon and chromium contents after the blow are 0.06% and 12.65%, respectively. The temperature of the bath after the blow is  $2018^{\circ}K$ .

The static model predicts (Table 6) carbon content as 0.061%, chromium content 13.10% and temperature  $2012^{\circ}K$ . The heat loss rate is found to be  $27\text{ K/min}$ .

The dynamic model predicts (Table 5) carbon content as 0.082%, chromium content 13.81% and temperature  $2022^{\circ}K$ . The average heat loss rate is found to be  $21\text{ K/min}$ . The average rate parameter is found to be  $0.08\text{min}^{-1}$  (contrast with  $0.09\text{min}^{-1}$  in earlier heats).

#### Heat No 4: AISI - 304 (Logsheet in Appendix D)

STAGE 1: The initial weight of the melt is 7050Kgs. The starting composition is: carbon=1.04% chromium=15.45%. The blow is continued for 42 minutes. The flow rate of oxygen and air used are  $4.6\text{ m}^3/\text{min}$  and  $0.75\text{ m}^3/\text{min}$ , respectively. During this blow, 520 kg of lime, 250 kg of high carbon ferro chrome are added. The additions are assumed to be made at the beginning of the blow (as advised by the operator). The initial temperature is assumed to be  $1773^{\circ}K$  for calculation. The experimental carbon and chromium contents after this blow are 0.14% and 14.84%, respectively. The experimental temperature is  $1930^{\circ}K$ .

The static model predicts (Table 8) carbon content as 0.174%, chromium content 11.37% and temperature  $1965^{\circ}K$ . The heat loss rate is found to be  $22.5\text{ K/min}$ .

The dynamic model predicts (Table 7) carbon content as 0.199%, chromium content 10.24% and temperature  $2009^{\circ}K$ . The heat loss rate is found to be  $18\ K/min$ .

Stage 2: The initial carbon and chromium contents are 0.14% and 14.84%, respectively and the initial temperature is  $1930^{\circ}K$ . The blow is continued for 12 minutes. The flow rate of oxygen and air used are  $2.8\ m^3/min$  and  $2.2\ m^3/min$ , respectively. During this blow, 5 Kg of aluminium is added to heat the metal (for raising temperature). This addition is assumed to be done at the beginning of the blow and reaction time is taken as approximately 1 minute. The experimental carbon and chromium after at the end of blow are 0.059% and 12.82%, respectively. The temperature of the bath after the blow is  $1985^{\circ}K$ .

The static model predicts (Table 8) carbon as 0.056% , chromium 13.26% and temperature  $2037^{\circ}K$ . The heat loss rate is found to be  $24\ K/min$ .

The dynamic model predicts (Table 7) carbon content as 0.098%, chromium 13.65% and temperature  $2053^{\circ}K$ . The heat loss rate is found to be  $18\ K/min$ . The average rate parameter is found to be  $0.05min^{-1}$ .

#### Heat No 5:AISI - 316(1) (Logsheet in Appendix E)

The initial weight of melt is 7600 Kg. The initial composition is: carbon 1.69%, chromium 19.10%. The blow is continued for 58 minutes. The flow rate of oxygen and air used are  $4.2\ m^3/min$  and  $1.2m^3/min$ , respectively. The initial temperature is assumed to be  $1743^{\circ}K$ . The silicon content of bath is 0.25%. By incorporating temperature rise and time required for oxidation of silicon, the starting temperature is found to be  $1753^{\circ}K$  and time of blow is corrected to be 54.27 minutes. During this blow 50 Kg of lime and 250 Kg of ferro-molybdenum are added. The additions are assumed to be made at the beginning of blow. The experimental carbon and chromium content after the blow are 0.07% and 14.03%, respectively. The temperature of bath is  $1978^{\circ}K$ .

The static model predicts (Table 10) carbon content as 0.13% and chromium content

13.76%, and temperature  $2062^{\circ}K$ . The heat loss rate is found to be  $19.5 K/min$ .

The dynamic model predicts (Table 9) carbon content as 0.2%, chromium content 15.39% and temperature  $2061^{\circ}K$ . The heat loss factor is found to be  $15 K/min$ .

### 4.3 Discussion

It would be observed from the results presented in Tables (1 - 10) that both static and dynamic models can be employed to predict end point conditions with almost equal degree of success. The actual and predicted values of carbon, chromium and temperature are plotted in Figures (4.4), (4.5) and (4.6), respectively. Standard deviations are: Carbon,  $\sigma = \pm 0.0358\%$ , chromium,  $\sigma = \pm 0.745\%$ , and temperature,  $\sigma = \pm 36.21^{\circ}K$ . In carbon range of 1.8% to 0.15%, the average value of rate parameter for carbon oxidation (for all the heats) is  $0.12 min^{-1}$ , which is slightly higher than  $0.09 min^{-1}$  (reported in the work of Fruehan[8]). In the carbon ranges of 0.15% and lower, the average value of rate parameter is  $0.09 min^{-1}$  (same as in the work of Fruehan[8]).

Considerable difficulty has been faced in this work in estimating the heat loss rate (expressed as  $K/min$ ) during each stage of operation because the thickness of refractory lining of AOD vessel varied from heat to heat and hence correct theoretical estimation of heat loss was not feasible. Estimated heat loss rates in different stages of the heats investigated in this work are plotted in Figure (4.7). It would be observed that the estimated values for both static and dynamic models vary in a broad range during different stages (minimum= $9.0 K/min$ , maximum= $27.0 K/min$ ). A more accurate estimation of heat loss rate during each stages will evidently result in a better estimate of bath temperature and chromium content. This is because oxidation of chromium is very sensitive to temperature. In earlier works[6] also maximum difficulty has been faced in prediction of temperature[6].

It is surprising to see that static model prediction are almost as good as the dynamic model in the last stage (within  $\pm 0.7\%$  chromium and  $\pm 0.04\%$  carbon). This is partly due

to the fact that heat loss rate has been used as an adjustable parameter. If a correct estimate of heat loss rate is made available, then the predictions from dynamic model are likely to be much more accurate than the static model. It is recommended to employ genetic adaptive search technique to simultaneously optimize the values of rate parameter for carbon oxidation ( $\sigma$ ), oxygen distribution factor ( $\beta$ ) and the heat loss adjustment factor (depending upon metal temperature and life of refractory lining) in the AOD converter. Seperate studies are already being conducted in this direction[10].



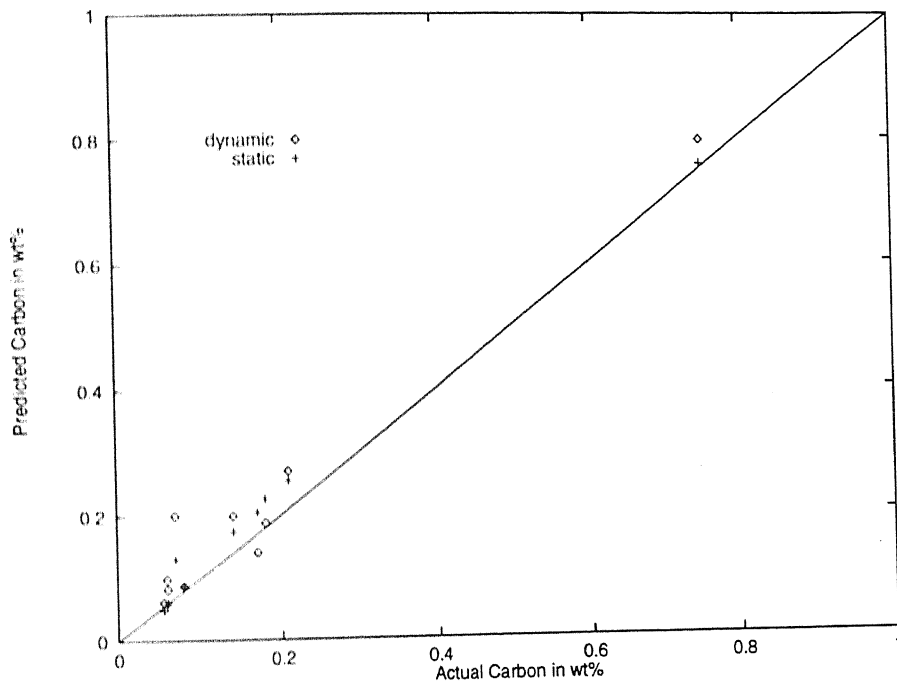


Figure 4.4: Comparison of predicted and actual carbon contents; Standard deviation:  $\sigma = \pm 0.0358$  and Correlation coefficient:  $R = 0.986$ ;  $\sigma_{dynamic} = 0.046$ ,  $R_{dynamic} = 0.9794$ ,  $\sigma_{static} = 0.0255$ ,  $R_{static} = 0.99$

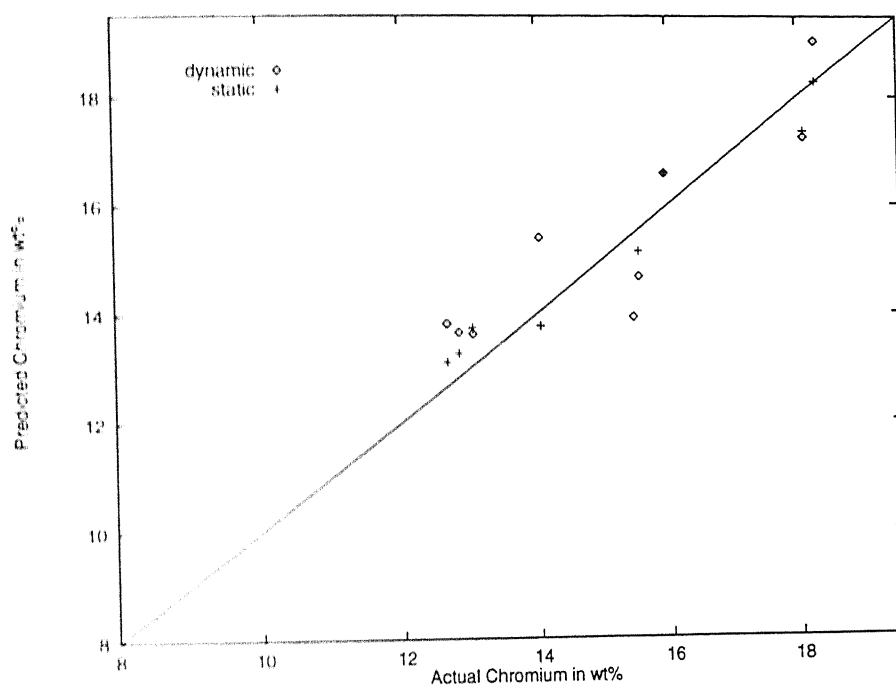


Figure 4.5: Comparison of predicted and actual chromium contents; Standard deviation:  $\sigma = \pm 0.745$  and Correlation coefficient:  $R = 0.925$ ;  $\sigma_{dynamic} = 0.778$ ,  $R_{dynamic} = 0.9309$ ,  $\sigma_{static} = 0.706$ ,  $R_{static} = 0.939$

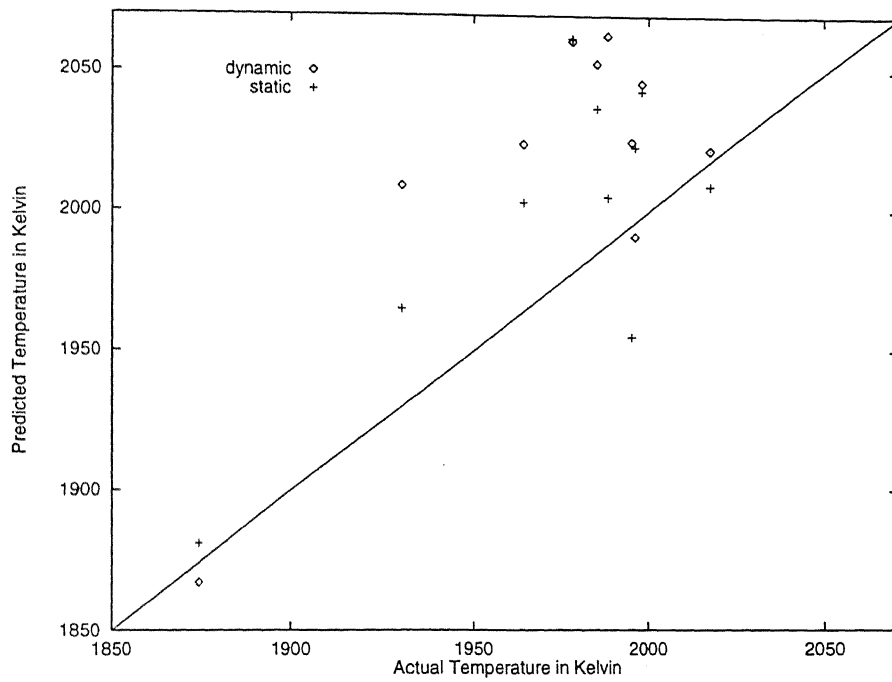


Figure 4.6: Comparison of predicted and actual temperature; Standard deviation:  $\sigma = \pm 36.21$  and Correlation coefficient:  $R = 0.7617$ ;  $\sigma_{dynamic} = 37.51$ ,  $R_{dynamic} = 0.7868$ ,  $\sigma_{static} = 36.47$ ,  $R_{static} = 0.7587$

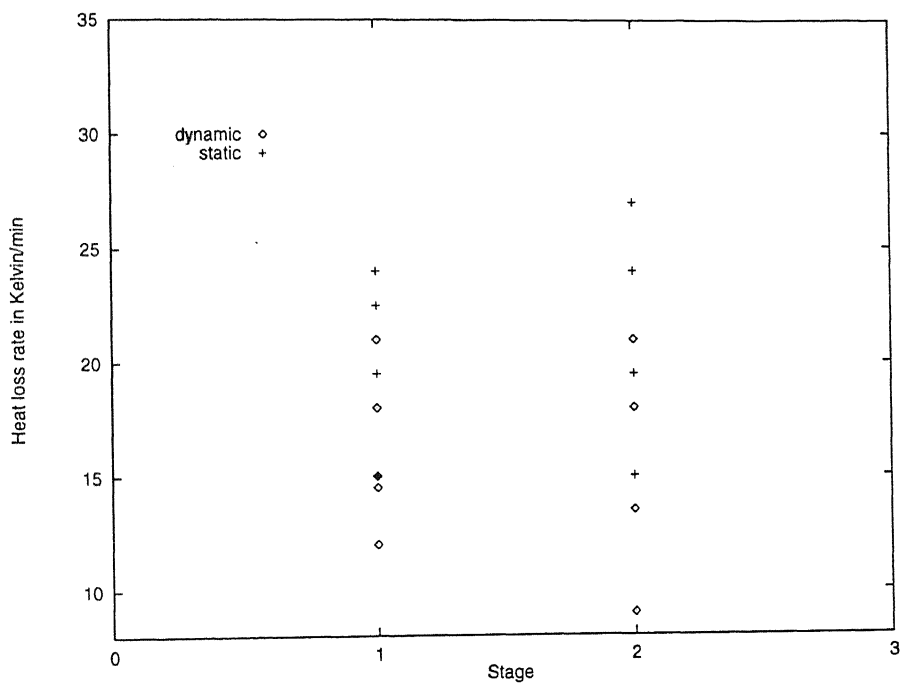


Figure 4.7: Heat loss rate: Heat loss rate (Kelvin/min) versus Stage

Table 1

DYNAMIC MODEL PREDICTIONS : STEEL - AISI 321, HEAT NO. I

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\sigma$ min <sup>-1</sup>	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
						Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	25	5.0	0.8	0.12	0.8	1.8*	0.75	0.796	19.80*	18.28	19.04	1743*	-	1867
2	34	5.0	0.8	0.12	0.8	0.75	0.18	0.188	18.28	15.54	14.67	1874*	1996	1991
3	22	1.8	3.3	0.09	1.0	0.18	0.055	0.061	15.54	13.03	13.62	1996	1995	2025

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
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1	-	12.0	
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2	Fe - Cr(H.C.) - 250 kgs.	21.0	
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	Fe - Mn(H.C.) - 100 kgs.		
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	Lime - 200 kgs.		
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3	Lime - 100 kgs	13.5	
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	Ni(P) - 250 kgs.		
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Table No 2

STATIC MODEL PREDICTIONS : STEEL - AISI 321, HEAT NO. I

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
					Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	25	5.0	0.8	0.8	1.8*	0.75	0.757	19.80*	18.28	18.28	1743*	-	1881
2	34	5.0	0.8	0.8	0.75	0.18	0.226	18.28	15.54	15.14	1874*	1996	2023
3	22	1.8	3.3	1.0	0.18	0.055	0.048	15.54	13.03	13.73	1996	1995	1955

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
-------	-----------	------------------------	--------

1	-	15.0	
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2	Fe - Cr(H.C.) - 250 kgs. Fe - Mn(H.C.) - 100 kgs. Lime - 200 kgs.	24.0	
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3	Lime - 100 kgs Ni(P) - 250 kgs.	19.5	
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Table 3

## DYNAMIC MODEL PREDICTIONS : STEEL - AISI 304, HEAT NO. II

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\sigma$ min <sup>-1</sup>	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
						Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	32	4.9	0.6	0.12	0.8	0.96	0.21	0.27	20.70	18.10	17.25	1880*	1998	2046
2	21	1.7	2.8	0.09	1.0	0.21	0.08	0.087	18.10	15.95	16.58	1998	1988	2063

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
1	Lime - 500 kgs. Fe - Mn(H.C.) - 95 kgs.	14.5	
2	scrap - 250 kgs	9.0	

Table 4

## STATIC MODEL PREDICTIONS : STEEL - AISI 304, HEAT NO. II

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
					Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	32	4.9	0.6	0.8	0.96	0.21	0.255	20.70	18.10	17.36	1880*	1998	2043
2	21	1.7	2.8	1.0	0.21	0.08	0.086	18.10	15.95	16.59	1998	1988	2005

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
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1 Lime - 500 kgs. 19.5

Fe - Mn(H.C.) - 95 kgs.

2 scrap - 250 kgs 15.0

123293



Table 5

## DYNAMIC MODEL PREDICTIONS: STEEL - AISI 316, HEAT NO. III

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\sigma$ min <sup>-1</sup>	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE °K		
						Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	50	5.0	1.25	0.12	0.8	1.29	0.17	0.14	14.50	15.45	9.33	1796	1964	2024
2	20	3.0	2.5	0.08	1.0	0.17	0.06	0.082	15.45	12.65	13.81	1964	2018	2022

\* – Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
1	<i>Lime</i> - 400 <i>kgs.</i> <i>Fe - Cr(H.C.)</i> - 740 <i>kgs.</i>	15.0	
2	-	21.0	

Table 6

## STATIC MODEL PREDICTIONS : STEEL - AISI 316. HEAT NO. III

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
					Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	50	5.0	1.25	0.8	1.29	0.17	0.205	14.50	15.45	13.92	1743*	1964	2003
2	20	3.0	2.5	1.0	0.17	0.06	0.061	15.45	12.65	13.10	1964	2018	2009

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
-------	-----------	------------------------	--------

1	Lime - 400 kgs.	15.0	
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	Fe - Cr(H.C.) - 740 kgs.		
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2	-	27.0	
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Table 7

## DYNAMIC MODEL PREDICTIONS : STEEL - AISI 304, HEAT NO. IV

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\sigma$ min <sup>-1</sup>	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
						Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	42	4.6	0.75	0.12	0.8	1.04	0.14	0.199	15.45	14.84	10.24	1743*	1930	2009
2	12	2.8	2.2	0.05	1.0	0.14	0.059	0.098	14.84	12.82	13.65	1930	1985	2053

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
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1	Lime - 520 kgs. Fe - Cr(H.C.) - 250 kgs.	18.0	
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2	Al - bar - 5 kgs	18.0	
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Table 8

## STATIC MODEL PREDICTIONS : STEEL - AISI 304. HEAT NO. IV

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\beta$	%CARBON			%CHROMIUM			TEMPERATURE ° K		
					Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	42	4.6	0.75	0.8	1.04	0.14	0.174	15.45	14.84	11.37	1743*	1930	1965
2	12	2.8	2.2	1.0	0.14	0.059	0.056	14.84	12.82	13.26	1930	1985	2037

\* -- Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
-------	-----------	------------------------	--------

22.5

1      Lime - 520 kgs.  
       Fe - Cr(H.C.) - 250 kgs.

24.0

Al - bar - 5 kgs

Table 9

## DYNAMIC MODEL PREDICTIONS : STEEL - AISI 316(1). HEAT NO. V

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	$\sigma$ min <sup>-1</sup>	3	%CARBON			%CHROMIUM			TEMPERATURE ° K		
						Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	58	4.2	1.2	0.12	0.8	1.69	0.07	0.2	19.10	14.03	15.39	1743*	1978	2061

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
-------	-----------	------------------------	--------

1	Lime - 50 kgs. Fe - Moli - 250 kgs.	15.0	
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Table 10

STATIC MODEL PREDICTIONS : STEEL - AISI 316L, HEAT NO. V

STAGE	TIME (min)	O <sub>2</sub> m <sup>3</sup> /min	AIR m <sup>3</sup> /min	3	%CARBON			%CHROMIUM			TEMPERATURE ° K		
					Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)	Initial	Final (Expt.)	Final (Pred.)
1	58	4.2	1.2	0.8	1.69	0.07	0.13	19.10	14.03	13.76	1743*	1978	2062

\* - Assumed value

STAGE	ADDITIONS	LOSS FACTOR ° K/min	REMARK
1	Lime - 50 kgs. Fe - Moli - 250 kgs.	19.5	

## Chapter 5

# Conclusions and Suggestions for Further Work

### 5.1 Conclusions

Static and dynamic models developed in this work have been successfully tested on actual plant data. It is found that carbon can be predicted with in  $\pm 0.0358\%$ , chromium with in  $\pm 0.74467\%$  and temperature with  $\pm 36.21^\circ K$ . In order to increase the accuracy of prediction, the heat loss rate must be estimated from refractory lining thickness. Since this information was not available and also the thickness of refractory varied from one heat to another, the prediction of temperature was not accurate ( $\sigma = \pm 36.21^\circ K$ ). Further, an alloy dissolution model must be developed and incorporated in the dynamic model. It is possible to integrate the dynamic model with cost optimization model so as to produce stainless steel at lowest cost.

### 5.2 Suggestions for Further Work

For some of the heats initial temperature and mass of steel was not reported in the logsheets and hence a reliable guess value was obtained by considering the possible rates of oxidation of chromium and carbon (as well as heat loss rate) observed in other heats. Estimated values have been marked by astrik (\*). Such difficulties are inherent in the operating

conditions existing on shop floor. An estimation (guess) procedure should therefore be standardized such that dynamic model automatically provides the default values where a particular value is not reported. In addition to this, an alloy dissolution model needs to be developed so that effects of changes in composition and temperature can be incorporated more accurately. Aspects of cost optimization can be utilized with the dynamic model so as to obtain stainless steel at lower cost.



# Heat No. I

TE: 17-02-96. HEAT NO:D1787. GRADE:AISI-321. SIZE:13"\*15",8"\*9".

TOTAL WEIGHT = LADLE METAL + SLAG WEIGHT = 8610kgs.

## M COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	*%Ti
0.08max	2.0max	1.0max	0.040max	0.040max	17-19	9-11	

17a.m. Heat transfered from furnace to AOD.

20a.m. First blow started.

Air	O <sub>2</sub>	Air
-	5.0	0.8.

45a.m. Stop blow.

47a.m. First sample taken out.

## COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.75	0.72	0.01	0.011	*0.41	18.28	1.83.

49a.m. Second blow started.

Air	O <sub>2</sub>	Air
-	5.0	0.8.

15a.m. ADDITIONS:

Fe-Cr(HC)	-	250Kgs.
Fe-Mn(HC) (LP)	-	100Kgs.
Lime	-	200Kgs.

23a.m. Stop blow.

24a.m. Second sample takenout.

## COMPOSITIONS:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.18	1.06	Tr	0.010	0.040	15.54	2.06

25a.m. Heat temperature - 1723°C.

26a.m. Thrid blow started.

Air	O <sub>2</sub>	Air
2.5	1.8	0.8.

2.35a.m. ADDITIONS:

Lime	-	100Kgs.
Ni(P)	-	250Kgs.

.48a.m. Stop blow.  
 .49a.m. Thrid msample taken out.

COMPOSITIONS:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.055	1.00	Tr	0.007	0.037	13.03	5.80

.50a.m. Heat temperature - 1722°C.

.52a.m. Fourth blow started.

Air	O <sub>2</sub>	Air
2.5	1.0	0.8.

.00a.m. ADDITIONS:

Lime	-	200Kgs.
Ni (P)	-	350Kgs.

Ar	O <sub>2</sub>	Ar
2.0	-	0.6.

.10a.m. ADDITIONS:

'Al' bar	-	11Kgs.
Lime	-	100Kgs.
Fe-Si (C) *	-	360Kgs.
Spar (fluospar)	-	25Kgs.
'Al' Shots	-	20Kgs.

.15a.m. Stop blow.

.16a.m. Fourth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.04	1.02	0.04	0.017	0.037	17.70	8.65

.17a.m. Fifth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.04	0.80	0.05	0.017	0.037	17.58	8.62

.18a.m. Heat temperature - 1724°C.

.35a.m. Slag off.

\*ADDITIONS:

Fe-Ti	-	100Kgs.
*	-	30Kgs.
Ni (P)	-	100kgs.

.39a.m. Heat temperature - 1678°C.

.42a.m. Last blow started.

Ar	O <sub>2</sub>	Ar
2.0	-	0.8.

.45a.m. Stop blow.

\* ADDITIONS:

*Fe-Cr	-	100Kgs.
*Me metal	-	60Kgs.
Ca-Si	-	12Kgs.
Fe-Bo	-	0.800Kgs.
Fe-Ti	-	*45Kgs.

.50a.m. Heat tapped.

\*\*\*\*\*

# APPENDIX - B

## Heat No. 2

DATE: -02-95. HEAT NO:D1783. GRADE:AISI-304. SIZE-13"\*15",  
8"\*9".

### AIM COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.08max	2.0max	1.00max	0.04max		18-21	8-10

12.50p.m. Heat transfer from furnace to AOD.

### LADLE SAMPLE REPORT:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
2.09	1.22	0.47	0.013	0.041	22.15	2.15

12.53p.m. First blow started.

Air	O <sub>2</sub>	Air
-	5.00	0.6.

01.15p.m. Stop blow.

" First sample taken out.

### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.96	0.92	Tr	0.016	0.037	20.70	2.10

01.18p.m. Second blow started.

Air	O <sub>2</sub>	Air.
-	4.9	0.6

### ADDITIONS:

Ca/Lime - 500Kgs.

Fe-Mn(M.C.) - 80Kgs+15Kgs=95Kgs.

01.50p.m. Stop blow.

" Heat temperature - 1725°C.

" Second sample taken out.

### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.21	1.05	Tr	0.013	0.036	18.10	2.2

01.54p.m. Third blow started.

Air	O <sub>2</sub>	Air
2.2	1.7	0.6.

" ADDITIONS:

Approx. 250Kgs. scrap taken.

02.15p.m. Stop blow.

" Heat temperature - 1715°C.

" Third sample taken.

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.08	1.12	Tr	0.005	0.035	15.95	2.50

02.18p.m. Fourth blow started.

Air	O <sub>2</sub>	Air.
2.2	1.2	0.6.

ADDITIONS:

Ca/Lime - Approx. 250Kgs.

Nickel plate - Approx. 350Kgs.

02.40p.m. Stop blow.

" Heat temperature - 1625°C.

" Fourth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.07	1.05	Tr	0.009	0.036	13.50	7.92

02.43p.m. Fifth blow started.

" Heat temperature - 1642°C.

Air	O <sub>2</sub>	Air.
-	2.8	0.6

ADDITIONS:

Ca/Lime - 150Kgs.

Fe-Si(L) - 350Kgs.

Nickel plate - Approx. 115Kgs.

Spar(fluospar) - 25Kgs.

'Al'shots - 25Kgs.

'Al'bar - 15Kgs.

02.50p.m. \*\*\* Argon 2.2 - 0.6.

02.57p.m. Fifth sample taken out.

" Heat temperature - 1652°C.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr
0.065	1.33	1.25	0.008	0.039	16.87
0.065	1.35	1.16	0.008	0.038	17.10

03.05p.m.

Slaf off.

"

A.O.D temp 1601°C.

%C	%Mn	%Si	%S	%P	%Cr
0.065	1.40	0.72	0.008	0.040	17.95

3.20p.m.

Heat tapping time.

Ladle temperature - 1539°C.

LADLE ADDITIONS:

L.C.Cr	-	50Kgs.
'Mn'metal	-	20Kgs.
Ca-Si	-	12Kgs.
Boron	-	800grams.
Nickel plate	-	60Kgs.

\*\*\*\*\*

# APPENDIX - C

## Heat No. 3

DATE: 21-01-96. HEAT NO: D1709. GRADE: AISI-316. SIZE: 23"\*27"+10"\*12"+4"\*5.5".

TOTAL WEIGHT=LADLE MELT+SLAG WEIGHT=8520Kgs.

### AIM COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.08max	2.00max	1.00max	0.040max	0.040max	16-18	10-14	2-3

2.00p.m. Heat transfered from furnace.

2.03p.m. First blow.

Air	-	O <sub>2</sub>	-	Air.
-		5.25	-	1.00.

2.05p.m. Stop blow.

2.06p.m. Heat temperature = 1523°C.

2.07p.m. First sample taken out.

### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
1.29	0.31	0.10	0.042	0.050	14.50	2.93	1.15.

2.10p.m. Second blow.

Air	-	O <sub>2</sub>	-	Air.
-		5.00	-	1.25.

### ADDITIONS:

2.30p.m. Fe-Cr(HC) - 400Kgs. Lime - 200Kgs.

2.40p.m. Fe-Cr(HC) - 340Kgs. Lime - 200Kgs.

3.00p.m. Stop blow.

3.02p.m. Heat temperature = 1691°C.

" Second sample taken out.

### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.17	0.10	Tr	0.041	0.047	15.45	2.84	1.86.

3.05p.m. Third blow started.

Air	-	O <sub>2</sub>	-	Air.
1.5		3.0		1.0.

3.25p.m. Stop blow.

3.26p.m. Third sample taken out.

### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.06	0.08	Tr	0.034	0.048	12.65	2.88	2.52.

3.30p.m. Fourth blow started.

Air	-	O <sub>2</sub>	-	Air.
2.5		1.5		1.0.

3.40p.m. Stop blow.

3.41p.m. Fourth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.045	0.12	Tr	0.028	0.048	11.61	2.91	2.50.

3.42p.m. Heat temperature = 1759°C.

3.43p.m. Fifth blow started.

Air	-	O <sub>2</sub>	-	Air.
2.5		1.5		1.0.

ADDITIONS:

3.45p.m. Ni(P) - 100kgs. Lime - 200Kgs.

3.50p.m. Ni(P) - 200Kgs. Lime - 200Kgs.

3.56p.m. Fifth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.04	0.14	Tr	0.028	0.047	10.45	5.45	2.47.

3.57p.m. Heat temperature = 1730°C.

3.58p.m. Sixth blow started.

Ar	-	O <sub>2</sub>	-	Ar.
1.75		0.85		1.0.

ADDITIONS:

4.00p.m. Ni(P) - 200Kgs. Lime - 200Kgs.

Ar	-	O <sub>2</sub>	-	Ar.
2.0		-		1.0.

4.10p.m. Ni(P) - 100Kgs. Lime - 100Kgs.

4.11p.m. 'Si'metal - 280Kgs. Spar(fluospar) - 25Kgs.

'Al'shots - 25Kgs. 'Al'bar - 10Kgs.

4.20p.m. Stop blow.

4.21p.m. Sixth sample taken out.

COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo.
0.044	0.29	0.54	0.033	0.047	16.15	10.10	2.17.



4.22p.m. Heat temperature = 1740°C.  
4.23p.m. Seventh sample Rejected.  
4.25p.m. Slag additions:  
Ni(P) - 50Kgs. Fe-Cr(LC) - 50Kgs. Fe-Mo(L) - 75Kgs.  
4.36p.m. Heat temperature = 1680°C.  
4.40p.m. Last blow started.  
  
Ar - O<sub>2</sub> - Ar.  
2.0 - 1.0.  
4.43p.m. Stop blow.  
ADDITIONS:  
'Si'metal - 20Kgs. Fe-Si(U) - 20Kgs.  
'Mn'metal - 100Kgs. Ca-Si - 12Kgs.  
4.45p.m. Tapping time.  
ADDITIONS:  
Fe-Ti - 12Kgs. Fe-Bo - 0.800Kgs.

\*\*\*\*\*

# APPENDIX – D

## HEAT NO. IV

### AOD PROCESS DATA

GRADE: AISI 304; WEIGHT OF MELT+SLAG=7050; DATE:08-02-96;  
SIZE: 13" \* 15"

#### AIM COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni
0.08max	2.00max	1.0max	0.050max	0.050max	18-21	8-10

#### LADLE SAMPLE REPORT:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Cu	%Co
1.04	1.22	0.09	0.027	0.037	15.45	9.42	0.22	1.10

#### TIME

#### ACTIVITIES AND DETAILS

05:20 a.m.

Heat transfered from f/c to A.O.D..

05:23 a.m.

1st blow started. Air - 02 - Air  
4.6 0.75

#### ADDITIONS:

Lime - 520 Kgs.  
Fe-Cr(H.C.) - 250Kgs.

06:05 a.m.

Blow stop.

06:08 a.m.

Sample taken.

#### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Cu	%Co
0.14	0.88	Tr	0.036	0.036	14.84	9.40	1.10	0.38

06:12 a.m.

Temperature - 1657 C.

06:13 a.m.

Second Blow started. Air - 02 - Air  
1.40 2.8 0.8

#### ADDITIONS:

Al bar - 5 Kgs.

06:25 a.m.

Blow stop.

06:27 a.m.

Temperature - 1712 C.

06:28 a.m.

Sample taken.

#### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Cu	%Co
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# APPENDIX – E

## HEAT NO. V

### AOD PROCESS DATA

GRADE: AISI 316(L); WEIGHT OF MELT+SLAG=7600; DATE:06-06-96;

SIZE: 14" \* 16"

#### AIM COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.03max	2.00max	1.0max	0.040max	0.040max	16-18	10-14	2-3

#### LADLE SAMPLE REPORT:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
1.69	0.6	0.25	0.012	0.033	19.10	3.05	0.36

#### TIME

#### ACTIVITIES AND DETAILS

07:42 a.m.

Heat transfered from f/c to A.O.D..

07:45 a.m.

1st blow started.    Air - O<sub>2</sub> - Air  
                                     -    4.2   1.2

#### ADDITIONS:

Ca/Lime        - 50 Kgs.  
Fe-Moli       - 250Kgs.

08:43 a.m.

Blow stop.

08:45 a.m.

Sample taken.

#### COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.07	0.23	Tr	0.011	0.028	14.03	3.10	2.34

08:47 a.m.

Temperature - 1705 C.

08:48 a.m.

Second Blow started.    Air - O<sub>2</sub> - Air  
                                     2.25   1.5   1.0

09:02 a.m.

#### ADDITIONS:

Lime - 150 Kgs.  
 09:12 a.m. Blow stop.  
 09:13 a.m. Temperature - 1636 C.  
 09:14 a.m. Sample taken.

## COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.045	0.27	Tr	0.09	0.015	13.96	3.08	2.52

09:15 a.m. Third Blow started.

09:30 a.m. ADDITIONS:  
 Lime - 50 Kgs.  
 Ni(P) - 570 Kgs.

09:30 a.m. Argon Blow started. Ar - 02 - Ar  
 2.5 - 1.0

09:33 a.m. ADDITIONS:  
 Lime - 50 Kgs.  
 Si Metal - 300 Kgs.  
 Spar - 250 Kgs.  
 Al Shots - 250 Kgs.

09:40 a.m. Argon Blow stop.

09:44 a.m. Sample taken.

## COMPOSITION:

%C	%Mn	%Si	%S	%P	%Cr	%Ni	%Mo
0.022	0.35	0.47	0.02	0.027	16.78	11.29	2.23

09:45 a.m. Temperature - 1756 C.

09:45 a.m. Sample taken.

09:48 a.m. Slag off.

## NOTE:

Heat spoiled due to electrical master control system fail.  
 So A.O.D. vessel going down. So total L.M. made skull in tapping pit.

# APPENDIX – F

## Composition of Ferroalloys

Alloy	%C	%Cr	%Mn	%Mo
High Carbon Ferro-chrome	7.0	60.20	–	–
High Carbon Ferro-manganese	7.0	–	80	–
High Carbon Ferro-molibdenum	7.0	–	–	80